

Solid Phase Extraction columns. A Coomassie Blue Assay was used to measure protein concentration before digestion and peptide concentration was determined by a Bicinchoninic Acid Assay after C-18 clean-up. Samples were pooled into four groups according to growth substrate and injected into a strong cation exchange column (SCX) which fractionated the sample into twenty-five fractions. Each of these fractions which represent a less complex mixture will then be analyzed by a reversed phase C-18 column coupled to an ion trap mass spectrometer used to detect and identify the peptides. Due to time constraints, however, mass spectrometric analysis will not occur until after the conclusion of this internship. All identifications will go into a reference peptide database/library and the results will be compared with mutations identified by previous genomic studies. If mutations are translated into proteins, mass spectrometry can then be used to identify the various strains of *E. coli*, drastically reducing both time and money. Future work may include preparing strains of *E. coli* grown on substrates other than glycerol and lactate for proteomic analyses.

**High-throughput Protein Purification.** DAVID ZHANG (*University of Illinois at Urbana-Champaign, Urbana, IL*); MIN ZHOU (*Argonne National Laboratory, Argonne, IL*). Structural genomics is an integral part of biology, where three-dimensional structures of macromolecules are determined using X-ray crystallography. As part of the Midwest Center for Structural Genomics, the Structural Biology Center (SBC) at Argonne National Laboratory has played a key role in developing protocols for cloning, protein purification, and structure determination. These three steps of the pipeline are linked in that order. Cloning determines which proteins are soluble enough and have optimal expression so that they may then be isolated by the purification group. Cells are grown to a certain density, which are then lysed. The cell extract is then purified through nickel-ion affinity chromatography. The target protein is then concentrated and set up for crystallization in a high-throughput manner. Crystals are then transferred over to the hands of the crystallographers where structure determination takes place by the multiple-wavelength anomalous dispersion (MAD) method. In the long-term, more cost-efficient methods and tools will be used in order to solve the more difficult projects. The two main issues that impede the structural genomics program are protein solubility and expression. Protein structures, especially those of important pathogens, may reveal a lot about the mechanisms in which they perform their functions. Discovering and analyzing protein structures are a major step towards the advancement of biomedical research.

**Characterization of Actin as a Cofactor for the Adenovirus Proteinase.** HAN ZHU (*Massachusetts Institute of Technology, Cambridge, MA*); WALTER F. MANGEL (*Brookhaven National Laboratory, Upton, NY*). A good model system for the development of effective protease-inhibition based anti-viral agents (drugs) is human adenovirus (AVP), because AVP is essential for the production of infectious viruses. AVP is found to require viral cofactors, which regulate the activity of AVP in time and space, for maximal activity. Actin, one of the most abundant proteins in the cell and a major component of the cytoskeleton, is believed to be an AVP cofactor due to the high homology of its c-terminus with the 11 amino acid peptide viral cofactor pVlc. The binding of monomeric actin to AVP allows for its activation and the cleavage and degradation of the cytokeatin-18 network of a host cell, releasing newly formed virions. Using a spectrofluorometric assay with optimized buffer conditions to preserve the native structure and monomeric form of actin, insights can be gained by characterizing the binding interaction between actin and AVP. Although the reaction rates were lower than expected, assays varying the actin concentration with constant concentrations of AVP suggest tight binding between actin and AVP. The KM of the AVP-actin complex was measured to be 7  $\mu$ M, very similar to the measured KM of the AVP-pVlc complex, suggesting that the binding of actin does not change substrate affinity. Rather, the binding of actin changes the properties of the enzyme itself, or the kcat (determined by VMAX). In addition, actin stimulates AVP in the presence of either one of the two viral cofactors (DNA and pVlc), allowing us to conclude that actin binds to two independent sites on AVP. Furthermore, through the use of competition assays with DNA, we were able to begin to estimate the binding affinity between actin and AVP with and without its viral cofactor pVlc. A better understanding of the interaction between actin and AVP should reveal new targets for anti-viral drug development.

## Chemistry

**Energetics of Electron Transfer and Charge Separation in Moderate to Low Polarity Solvents.** BRIAN ALBERT (*Columbia University, New York, NY*); JOHN MILLER (*Brookhaven National Laboratory, Upton, NY*). Because photosynthesis occurs in a region

of low polarity so that photoelectrons store their absorbed energy in new chemical bonds instead of emitting it as heat through interaction with the solvent, studying electron transfer and charge separation in low polarity solvents will have applications in new solar energy storage. These experiments combine strong electron donors (metalloenes) and strong electron acceptors (quinones) to obtain ion formation by thermal equilibria in media of moderate to low polarity. In solvents of a range of dielectric constants, the extent to which cobaltocene and various quinones formed ion pairs and separated to form free ions was measured via conductivity and UV-Vis spectroscopy. Gibbs free energy changes were calculated for both the electron transfer and charge separation reactions in various solvents using acetonitrile as a standard highly polar solvent. With known values for the ionization potential of cobaltocene and the electron affinities of the quinones, Gibbs free energy changes observed in the moderately polar solvent, tetrahydrofuran (THF), were fit to the theoretical Born solvation energy and Coulomb potential models. Predictions made for free energy changes in solvents of very low dielectric constants disagreed with experimental data because a fourth species, charge transfer complex, becomes more significant in relative concentration, thus introducing a third equilibrium. Also, molecule structure of the solvent molecule was found to affect Gibbs free energy changes of ion formation. Approximations of neutral specie, ion pair, and free ion concentrations became more difficult in low polarity solvents because of charge transfer complexes that appear as broadened peaks in UV-Vis absorption spectra as well as extremely low conductivity measurements. Observed Gibbs free energy changes were found to be significantly more unfavorable compared to redox potentials of the same reactions determined electrochemically. The difference is attributed to the stabilization caused by salt in solution required for the electrochemical method.

### Selective Electrochemical Oxidation of Sodium Chloride

**Solution.** MAX BASTOW (*Colorado College, Colorado Springs, CO*); CHARLENE SANDERS (*Oak Ridge National Laboratory, Oak Ridge, TN*). Activated electrodes placed in saline solution create an electric double layer composed of opposite charges, repelling ions of like charge. It is hypothesized that, due to this characteristic of the electric double layer, it is possible to inject a short anionic pulse into a saline solution that will selectively oxidize water to produce oxygen. If the pulse is short enough, it will stop before chloride ions are drawn to the electrode surface, thus avoiding production of chlorine. This would have applications to the generation of oxygen and hydrogen from sodium chloride solutions. Phosphate buffered saline (PBS) was placed into an electrolysis cell and a stimulus generator was used for controlled charge injection of an anionic pulse. This pulse was applied for 4 hours in a closed cell and chlorine production was observed by the spectrophotometric determination of hypochlorite based on its reaction with ascorbate. The same pulses were then applied to an identical cell containing PBS sparged with N<sub>2</sub> at 50 ml/min. A galvanic cell was used for oxygen measurements, and a Figaro gas sensor was used for hydrogen measurements. Evolution of chlorine was not observed until pulse widths greater than 200  $\mu$ s were applied. At this pulse width the production of oxygen was already well established at  $0.11 \pm 0.01$   $\mu$ mol/hr. At the greatest applied pulse width of 400  $\mu$ s chlorine production was at  $0.053 \pm 0.008$   $\mu$ mol/hr while oxygen production was  $0.25 \pm 0.01$   $\mu$ mol/hr. These results show that short pulses are indeed capable of oxidation of water in PBS to produce oxygen while avoiding the oxidation of chloride to chlorine.

### Electrochemical Arsenic Remediation of Drinking Water in Rural Bangladesh.

YOLA BAYRAM (*University of Michigan – Dearborn, Dearborn, MI*); ASHOK GADGIL (*Lawrence Berkeley National Laboratory, Berkeley, CA*). According to the World Health Organization, in Bangladesh over 60 million people drink arsenic-laden water making it the largest case of mass poisoning in human history. Available methods of treating arsenic are too expensive, ineffective, or commonly difficult to implement, making them unsuitable for a poor or undeveloped country such as Bangladesh. Electrochemistry may provide an innovative, effective, and inexpensive method for arsenic remediation of drinking water. The method is an improvement upon a known method of using Fe(III) to remove arsenic. The Fe(III) combines with As(V), forming an insoluble complex which then can be easily filtered out. The innovative step of electrochemistry allows control over the amount of Fe(III) produced as well as electrochemical oxidation of the As(III) into reactive As(V) anion, making the method far more effective. Experiments were performed with water samples with 600ppb of total arsenic that received various amounts of current for varying durations of time. The objective is to determine the appropriate current and time necessary for an arsenic removal below 50ppb in order to meet

Bangladesh standards. It was found that a charge between 96.35C/L and 103.76C/L gave an arsenic concentration within the range or below the Bangladeshi standard. Once the process is well understood and the electrochemical variables are optimized, the method will be applied to a practical water filter. The hope is that this filter will be applied in Bangladesh and other areas affected by arsenic poisoning to provide millions of people with safe drinking water and an improved standard of living.

**Metabolism of Dibromoacetic Acid and Bromochloroacetic Acid by Rat Liver Cytosol.** ANNA BEILER (*Messiah College, Grantham, PA*); IRVIN SCHULTZ (*Pacific Northwest National Laboratory, Richland, WA*). Di-halogenated acetic acids (di-HAAs) are common by-products of municipal disinfection of drinking water and are known rodent hepatocarcinogens. Concern has been voiced by environmental and regulatory agencies about their effects in humans. In this study, the *in vitro* metabolism of two di-HAAs, dibromoacetic acid (DBAA) and bromochloroacetic acid (BCAA), was measured. The kinetics of DBAA and BCAA metabolism was studied in young male and female rat liver cytosol. The metabolism was characterized by both consumption of added substrate and formation of the initial metabolite, glyoxylate, after 1–30 minutes incubation at 37°C. Both the di-HAAs and glyoxylate were quantified by conversion to their respective methyl esters and subsequent analysis by gas chromatography-mass spectroscopy (GC-MS). BCAA is a chiral compound and its stereoisomers were analyzed using a chiral column on a GC-electron capture detector (GC-ECD). Due to technical difficulties with methylation of glyoxylate and analysis by GC-MS, conclusive data for the DBAA experiment was not found. In the BCAA incubations, the (-) BCAA stereoisomer was consumed so rapidly it was impossible to obtain a conclusive rate of metabolism. Further studies should repeat the experiment at a slower rate. Also, the method should be further developed to work more accurately on the brominated haloacids. In addition, future studies can explore the kinetics of remaining di- and tri-halogenated acids, and apply the findings to the effects on humans at the concentrations found in drinking water.

**Kinetic Studies of Ammonia Borane.** STEPHEN BERDS (*Monroe Community College, Rochester, NY*); WENDY SHAW (*Pacific Northwest National Laboratory, Richland, WA*). The need for effective hydrogen fuel cells (HFCs) is paramount to the success of establishing a stable energy economy based on hydrogen. At the heart of a productive HFC lies a system for efficiently storing and releasing hydrogen in a controlled fashion. One promising method for such a system is to use chemicals to store hydrogen. Ammonia borane,  $\text{NH}_3\text{BH}_3$  (AB) is both stable at room temperature and, with modest heating, able to generate hydrogen ( $\text{H}_2$ ) with an  $\text{H}_2$  to AB ratio of greater than 2:1. To better understand the effect which temperature has on the release of  $\text{H}_2$  from AB, a gas burette system was employed to measure the amount of  $\text{H}_2$  released from AB at set temperatures over time. AB was also loaded on MCM-41, a mesoporous scaffold, in several different mass ratios with AB to study its effect on  $\text{H}_2$  release. It was found that the induction period which exists to release one mass equivalent of  $\text{H}_2$  is directly dependent on the reaction temperature. The second mass equivalent of  $\text{H}_2$  which is released does not have a separate induction period and is generated at only slightly higher temperatures than the first equivalent. The addition of MCM-41 both increased the rate of hydrogen release and eliminated the induction period for the release of the first equivalent of  $\text{H}_2$ . This research is part of a larger study being conducted by the Department of Energy's Chemical Hydrogen Storage Center for Excellence to fully characterize the mechanism and kinetics of  $\text{H}_2$  release from AB. This work was supported by the Office of Energy Efficiency and Renewable Energy of the Department of Energy.

**Electrolysis of Saline for pH Control and Oxygen Production.** ANNA BESMANN (*University of North Carolina at Asheville, Asheville NC*); ELI GREENBAUM (*Oak Ridge National Laboratory, Oak Ridge, TN*). Diabetic retinopathy is a disease which causes small, fragile blood vessels to form within the retina to compensate for the normal blood vessels' inability to bring sufficient oxygen to the eye. These blood vessels are prone to hemorrhaging in the eye, causing temporary or permanent blindness. To help stop this problem before the small blood vessels can form, electrodes can be implanted into the eye to stimulate the production of oxygen in the vitreous humor. However, this also induces the formation of free chlorine, which causes the vitreous humor to become more alkaline. In order to keep the pH at a manageable level, an anode and a cathode can be implanted into the vitreous humor while a second anode connected to both electrodes by a sidearm can be implanted behind the ear. Protons will pass back and forth along the sidearm, keeping the vitreous humor from becoming too acidic or too

alkaline. Alternating between both configurations keeps the pH stable, as the internal electrodes cause a rise in pH while the sidearm electrode causes a drop in pH. In these experiments, two electrodes were put into the buffered saline itself and a third electrode into a glass sidearm filled with saline solution. To counter the problem of excessive baseline pH shift, a 2 mM solution of phosphate buffered saline (PBS) was used instead of pure saline. The solution was sparged at 25 ml/minute and heated with a water bath to 37°C to simulate the fluid motion in the vitreous humor and temperature of the human body. A DC charge of 800  $\mu\text{A}$  was applied to the electrodes to stimulate the production of oxygen and a change in pH. The internal electrodes were used in three minute increments until the pH had moved one pH unit above the baseline, then the sidearm electrode was used in 1.5 minute increments to bring the pH down 2 units. Afterward, the internal electrodes were used to bring the pH back to the baseline. However, the exact amount of time needed to reach the acceptable limits of high and low pH was variable, and on occasion use of the internal electrode after using the sidearm electrode for a long period of time caused the pH to drop for unknown reasons. The next step of this process would be to repeat the experiment with a solution that is more like the vitreous humor of the eye, and eventually move on to implanting the electrodes within an actual eye.

**Multiplexed Assemblies for SERS-Detection Applications.** CHRISTINA BRADY (*University of California – San Diego, San Diego CA*); STEPHEN DOORN (*Los Alamos National Laboratory, Los Alamos, NM*). Raman techniques offer advantages over the well-established fluorescence in detection applications and microscopic analysis. Unlike fluorescence, Raman spectroscopy generates narrow peak widths allowing for a distinct fingerprint spectrum and easy identification of a material; however, low signal strength from Raman spectroscopy has limited its practical applications. Raman applications have increased with the use of Surface Enhanced Raman Scattering (SERS). To overcome weak signal strength, metal nanoparticles, such as gold or silver, are used as substrates for the attachment of the signal dye. Various attempts have been made to optimize the Raman signal by allowing the combination of different signal dyes for a single SERS-active nanoparticle. To achieve this, current research at Los Alamos National Laboratory involves synthesis of multiplexed nanoparticle assemblies to give a combination of signals. Silver (Ag) nanoparticles approximately 60nm in diameter were tagged with a particular Raman dye, aggregated, and silica coated. The tagged Ag particles were attached to silicon microspheres via biotin-avidin interactions in different dye ratios. Raman spectroscopy and Raman microscopy were used to measure and characterize the signal strength of the particles. Results showed that optimization of Raman signals occurred with the aggregation of Ag nanoparticles due to increased surface plasma resonance between the particles. Attachment chemistry of SERS-active nanoparticles to the silicon bead and dye combination spectra are currently being analyzed. Multiplexed nanoparticles can be used in further experiments requiring SERS-detection of different substrates simultaneously. Future synthesis of multiplex particles with different combination of dyes will allow for a larger array of dye spectra than currently available.

**Synthesis of Silicon and Gold Nanoparticles.** ROBERT BROWN, MORGAN McGRAY (*Western Kentucky University, Bowling Green, KY*); MARVIN G. WARNER (*Pacific Northwest National Laboratory, Richland, WA 99352*). Gold and silicon nanoparticles have been widely used for their unique characteristics for various applications. By attempting to replicate other researchers' work, these syntheses were explored and expanded upon. Using sodium naphthalide in 1,2-dimethoxyethane as a reducing agent, adding silicon tetrachloride, and finally capping with octanol gives octanol-capped silicon nanoparticles. Gold nanoparticles can be synthesized through the use of hydrogen tetrachloroaurate(III) hydrate, toluene, and tetraoctylammonium bromide. With the addition of triphenylphosphine, the gold particles can be stabilized. In addition, ligand exchange reactions can be carried out with 4-trifluoromethylbenzenethiol to produce nanoparticles with varying functionalities. It is evident that the gold nanoparticles are more easily produced and more stable than their silicon counterparts. Although we were not able to test the purity of our gold particles with  $^1\text{H}$  NMR, thin layer chromatography (TLC) showed high purity. The silicon nanoparticles were found to aggregate and were different than what was anticipated based on the reported literature preparation.

**Isolation and Analysis of Above Cloud Point Precipitates in Palm and Poultry Fat Derived Biodiesels.** REBECCA CALLAHAN (*Hendrix College, Conway, AR*); TERESA ALLEMAN (*National Renewable Energy Laboratory, Golden, CO*). As the search for alternatives to petroleum based fuels continues many promising options have arisen. Vegetable



and animal fat derived biodiesels have become one viable alternative to petroleum based diesel fuel. Biodiesel can be directly substituted for petrodiesel while exhibiting less hazardous and superior environmental properties, such as its high flash point and biodegradability. Biodiesel typically has high cloud and pour points than conventional diesel. Additionally, a small fraction of biodiesels also show a precipitate formed above the cloud point. This precipitate may accumulate in storage tanks or on fuel filters inhibiting biodiesel's distribution. The identification of this precipitate may assist in finding a solution to its operability problems or an identification method of the fuels it impairs, thus enhancing the capability of biodiesel as an alternative fuel. Multiple samples of biodiesel were visually examined for the presence of precipitate at room temperature and two samples of different feed stocks were chosen for precipitate analysis, one palm and one poultry fat. Three steps were implemented to identify their precipitates. First, the mass of precipitate was increased by chilling biodiesel above its cloud point. The precipitate was then isolated from biodiesel through filtration and solvent washing. Lastly it was identified using the following analytical techniques: Fourier Transform Infrared Spectroscopy (FT-IR), Gas Chromatography Flame Ionization Detector (GC-FID) pyrolysis Molecular Beam Mass Spectrometry (py-MBMS), and proton, carbon 13 and Distortionless Enhancement by Polarization Transfer Nuclear Magnetic Resonance (H NMR and  $^{13}\text{C}$  NMR and DEPT NMR.) Using these methods of analysis it was determined that the two samples differed in physical appearance, yet both contained a large quantity of monoglycerides. Approximately ten percent of the samples examined in this work showed precipitation upon cooling, additional examination of biodiesels needs to be conducted to verify that this precipitation is universal to all feed stocks. Additionally, after the definitive identification of the precipitates, their impact on fuel filters must be quantified from the distributor to the vehicle.

**BOB Ionic Liquids: Preparation and Properties.** ALEJANDRA CASTANO (Queens College, Flushing, NY); JAMES WISHART (Brookhaven National Laboratory, Upton, NY). Ionic liquids (ILs) are salts that melt below  $100^\circ\text{C}$ . ILs are ideal alternative solvents to work with because they exhibit properties such as thermal stability, non-volatility, combustion resistance, high conductivity, and wide electrochemical windows. Owing to their non-volatility ILs do not contribute to air pollution and they are being investigated for a variety of applications as alternative solvents, including use in nuclear processes. The potential utility of ionic liquids for the processing of radioactive material is being investigated through the use of pulse radiolysis techniques. Ionic liquids containing the Bis(Oxalato)Borate (BOB-) anion are being investigated for this application, because of the neutron scavenging ability of 10boron. Calculations by others have shown that ILs containing boron can be used to handle higher concentrations of fissile material than conventional solvents without the risk of criticality. Halide salts such as 1-methyl-3-pentylimidazolium bromide (C5MIM Br) and a homologous series of pyrrolidinium, and pyridinium types were synthesized using both thermal and microwave-assisted techniques. The halide salts were prepared by reacting the amines with their corresponding alkyl halides. Boron containing ILs were prepared by metathesis reactions with sodium BOB (NaBOB). NaBOB was synthesized by reacting boric acid, oxalic acid and sodium hydroxide in water under reflux conditions. Preliminary results of pulse radiolysis experiments indicate that BOB anion scavenges radiolytically-generated solvated electrons too efficiently for BOB ILs to be stable as neat solvents for processes under ionizing radiation, as in nuclear separations. Thus, only small concentrations of borated ILs such as the BOB salts may be necessary to achieve inherent criticality protection. The salts would be most effective when dissolved in a IL co-solvent such as N-butyl-N-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide. Further characterizations such as viscosity, melting points, glass transitions, and electrochemical windows are also being investigated. Such data will provide valuable information to facilitate the broader applications of the BOB ILs.

**Characterization of Silicon Carbide for Water-Splitting and Corrosion Protection.** BORIS CHERNOMORDIK (University of Louisville, Louisville, KY); JOHN TURNER (National Renewable Energy Laboratory, Golden, CO). Harnessing hydrogen as an energy carrier by means of renewable power, such as solar, is key to achieving a clean and dependable energy cycle. Direct photoelectrolysis of water with photoelectrochemical (PEC) cells is the most efficient method to collect hydrogen from water. In this study, commercial samples of the 4H polytype of silicon carbide (SiC), with n- and p-type doping, were photoelectrochemically characterized with a focus on durability for possible use as a protective coating for chemically sensitive high-efficiency PEC materials. The indirect band gap was found to agree

with the literature value of  $3.23\text{eV}$  and the bands were found to straddle the water electrolysis redox potentials, with the flat band potential vs. pH relationship exhibiting Nernstian behavior. Corrosion experiments showed that n-type SiC is susceptible to oxidative etching, while p-type SiC did not show signs of corrosion. Though the high band gap renders 4H-SiC inefficient for photoelectrolysis because it absorbs only a tiny portion of the solar spectrum, corrosion experiments suggest that p-type SiC may be durable enough to act as a protective layer in PEC cells. More experimentation in this regard is necessary, though. In addition, more research is needed into methods for incorporating SiC as a protective coating for a high conversion efficiency cell.

**\*Design and Development of Palladium-Iron Bimetallic Electrocatalysts for Polymer Electrolyte Fuel Cells.** RICHARD COOK, JESSICA PRICE (Berea College, Berea, KY); MARK CUNNINGHAM (Argonne National Laboratory, Argonne, IL). The path to more efficient energy sources for modes of transportation, to replace the  $\text{CO}_2$ -emitting, low efficiency internal combustion engine, has led The Department of Energy and Argonne National Laboratory to develop commercially competitive polymer electrolyte fuel cells (PEFCs). The purpose of this project is to design and develop bimetallic cathodic electrocatalysts for PEFCs with high electrochemical activity and high stability in order to replace more expensive platinum-based electrocatalysts. The bimetallic electrocatalysts reported in this study are composed of the precious metal palladium (Pd) and the base metal iron (Fe) fixed onto carbon support. The less expensive base metal, iron, is designed to comprise the core of the bimetallic alloy with a monolayer outershell consisting of palladium. The Pd-Fe electrocatalysts were synthesized by the impregnation method, utilizing  $\text{Fe}(\text{NO}_3)_3$  and  $\text{Pd}(\text{NO}_3)_2$  as metal precursors, producing bimetallic catalysts with a range of metal compositions. The precursor salts were reduced to the Pd-Fe bimetallic electrocatalyst in a dilute hydrogen atmosphere. Transmission electron microscopy, temperature programmed-reduction, and cyclic voltammetry, using the rotating disk electrode, were used to characterize the electrocatalysts' composition and particle size, reduction conditions for heat treatment, and catalyst stability and performance, respectively. The bimetallic catalyst with a molar ratio of 30:70 (Pd:Fe), heat treated in regen gas at  $620^\circ\text{C}$  for 10 hours, showed the highest activity of  $65.31\text{ mA/mgPd}$  at  $0.85\text{V}$ . Further research will focus on maximizing catalyst performance by optimizing heat treatment conditions to minimize particle size with a core-shell morphology. The desired end result is a bimetallic alloyed electrocatalyst that is cost efficient, has a high rate of oxygen reduction, a small particle size, and an activity of  $440\text{ mA/mg metal}$  at  $0.9\text{V}$  (2010 DOE target).

**Seeding Nucleation for the Production of Diamond Stripper Foils.** RYAN COLEMAN (The University of Virginia, Charlottesville, VA); ROBERT W. SHAW (Oak Ridge National Laboratory, Oak Ridge, TN). Diamond stripper foils are implemented by the Spallation Neutron Source (SNS) to convert  $\text{H}^-$  to  $\text{H}^+$  at the entrance of the accumulator ring. These corrugated nanocrystalline diamond foils can currently withstand about  $800^\circ\text{C}$  of injected charge when exposed to the 20 Hz, 800 MeV Proton Storage Ring at Los Alamos National Laboratory. Currently, it is necessary for the stripper foils to have lifetimes in excess of 200 hours for the operational scheduling of the SNS system to be independent of foil lifetimes. In light of the scheduled power upgrade for the SNS accelerator, research in producing stripper foils with longer lifetimes is necessary for the efficient operation of the SNS facility. Essentially, the production of diamond films involves two major steps: nucleation and growth. My research has been conducted to develop a nucleation procedure that is similar to one that recently appeared in the literature. The diamond films are grown on silicon substrates, and previously, nucleation sites were created by scratching the substrate surface in a diamond slurry solution. The new nucleation process involves depositing an amorphous carbon layer on the silicon substrate and then sonicating a dense layer of nano-powder diamond particles into the amorphous layer. These diamond particles act as seeds during the growth process, and the hypothesis was that this nucleation process could produce diamond films with higher uniformity. The amorphous carbon layers were deposited on the substrate surfaces with microwave plasma assisted chemical vapor deposition, and over the course of many experiments, the deposition variables were adjusted to find the ideal conditions for seeding. The varied experiments showed that the experimental apparatus could not yield the uniformity and thickness reported in the literature. However, we have discovered that the amorphous carbon layer may not be necessary; simply seeding the silicon substrates can promote the growth of uniform diamond films. The apparatus has no independent heating source, and the substrate temperature variable is strongly coupled with the power and pressure variables. This coupling prevented reproduction of the

reported growth conditions, and the reported nucleation process could not be implemented within the confines of the apparatus. As a result, the next phase of the research project is to incorporate an independent heating source into the plasma chamber.

**\*Fuel Cells: Synthesis and Characterization of Sulfonated Polysulfone for Proton Exchange Membrane (PEM).** NANCY DAVENPORT (Chicago State University, Chicago, IL) ASARE NKANSAH (Argonne National Laboratory, Argonne, IL). Fuel cells are electrochemical energy conversion devices which convert hydrogen and oxygen into water in the process of generating electricity. The most common fuel cells are proton exchange membrane fuel cells (PEMFC). In order to develop newer proton exchange membrane (PEM) material, a monomer containing protogenic sulfonic acid groups on the pendant branches was prepared from commercially available 2,2'diallylbisphenol A via two different reactions. The course of the reaction was followed by thin layer chromatograms. This new monomer was then polymerized with 4, 4'-dichlorodiphenyl sulfone by step growth polymerization. The resulting polymer was characterized by NMR. The most striking feature of this new polysulfone was its extremely high decomposition temperature. Future work involves conductivity and viscosity measurements to determine the application of sulfonated polysulfone as (PEM) in fuel cells.

**Synthesis of Dendrimeric Polysulfonic Acid for Use as a Proton Exchange Membrane.** BRIAN DAVIS (Chicago State University, Chicago, IL); SUHAS NIYOGI (Argonne National Laboratory, Argonne, IL). The fuel cell technology is an alternative energy/power for the future. The performance of a proton exchange membrane fuel cell is dependent upon the ability of the membrane to transport protons from the anode to the cathode. The current technology uses expensive perfluorinated sulfonated polymer like Nafion with limitations. In this work a new hyperbranched sulfonated polysulfonate was prepared for possible application as a membrane material. Due to its inherent structure and the presence of sulfonic acid groups on the outer part of the polymer it is expected to provide efficient proton transport. The monomer 2-hydroxy-4-methyl-benzene-1,3-disulfonyldichloride (HDDC) was synthesized by reacting m-cresol in large excess of chlorosulfonic acid at room temperature. The monomer was polymerized via self-condensation in a biphasic system. The polymer was hydrolyzed to free sulfonic acid to obtain water soluble product. Insoluble hyperbranched polymer was obtained by reacting with 4,4-dihydroxybiphenyl prior to hydrolysis. The polymer melted at around 215–225°C.

**Physical and Chemical Properties of Polyol-Based Deicing Solutions.** SARINA DORAZIO (Genesee Community College, Batavia, NY); WILLIAM D. SAMUELS (Pacific Northwest National Laboratory, Richland, WA). The U.S. Environmental Protection Agency (EPA) regulations require an alternative for the environmentally toxic propylene glycol (PG) and organic salt based deicers currently used in the United States at an estimated 35 million kg annually. New Battelle derived polyol-based deicing solutions are a more environmentally friendly, materials friendly, and cost effective alternative to PG or organic salt based deicers for airplanes and runways. The polyol-based solutions produced are D3: Degradable by Design Deicers, which include both Airplane Deicing Fluid (ADF) and Runway Deicing Fluid (RDF). These solutions meet the criteria put forth by different U.S. regulatory agencies such as the Federal Aviation Administration (FAA), EPA, and Department of Defense (DoD). Quick, reliable and simple testing parameters are critical to the eventual use of these solutions. Due to these constraints, a number of measurements were performed between June and August 2007 on various dilutions of the certified ADF and RDF solutions in order to define certain characteristics: refractive index, pH, density, and freezing point. A freezing point apparatus was used which was assembled to meet American Society for Testing and Materials (ASTM) specifications. Freezing points and other physical tests were run on diluted certifiable fluids and the data was correlated to identify the tests that will best predict the composition and efficacy of the fluid. Various cooled solutions were investigated with respect to their ability to transfer heat both quickly and efficiently in the freezing point apparatus.

**Large Scale Production, Purification, and  $^{65}\text{Cu}$  Solid State NMR of Azurin.** AMY GAO (Olin College of Engineering, Needham, MA); ROBERT HECK (Pacific Northwest National Laboratory, Richland, WA). This paper details a way to produce azurin with an efficiency over 10 times greater than previously described and demonstrates the first solid state nuclear magnetic resonance spectrum of  $^{65}\text{Cu}(\text{I})$  in a metalloprotein (Harris *et al.*, 2004). A synthetic gene for azurin based upon the DNA sequence from *P. aeruginosa* including the periplasmic targeting sequence was subcloned into a T7 overexpression vector

to create the plasmid pGS-azurin, which was transformed into BL21 (DE3) competent cells. The leader sequence on the expressed protein causes it to be exported to the periplasmic space of *Escherichia coli*. Bacteria grown in a fermentation unit were induced to overexpress the azurin, which was subsequently purified through an endosmotic shock procedure followed by high performance liquid chromatography (HPLC). 1,480 mg of azurin were purified per liter of culture.  $^{65}\text{Cu}(\text{II})$  was added to apo-azurin and then reduced. The  $^{65}\text{Cu}$  metal cofactor in azurin was observed with solid state nuclear magnetic resonance (NMR) to determine any structural variations that accompanied copper reduction. This is the first ever solid state NMR spectra of a copper(I) metalloprotein. Analysis of the NMR spectra is being used to complement hypotheses set forth by X-ray diffraction and computational calculations of electron transfer mechanisms in azurin.

**Characterization of Non-platinum Electrocatalysts for Polymer Electrolyte Fuel Cells.** JAMES GILBERT (University of Illinois at Chicago, Chicago, IL); XIAOPING WANG (Argonne National Laboratory, Argonne, IL). Two of the limiting factors for polymer electrolyte fuel cell (PEFC) development are the cost and supply availability of platinum, which is currently used as the electrocatalyst for both the oxygen reduction reaction (ORR) and the fuel oxidation reaction. The goal of this project is to develop ORR catalysts that do not contain platinum, are less expensive, and offer comparable ORR activity to platinum-based catalysts. In this work, a testing procedure was established to evaluate ORR activity by using commercial platinum and non-platinum electrocatalysts and using cyclic voltammetry with a rotating disk electrode setup that is used for correction for mass transport contribution. The non-platinum catalysts studied were different compositions of a palladium-based bimetallic system supported on carbon that were prepared by impregnation and post-temperature-programmed reduction. Their ORR activity per mass of metal catalyst was determined and compared to that of commercial catalysts. Results show that the alloying of the base metal to the palladium yields a greater activity. The best ORR activity was observed from the atomic ratio of palladium to the base metal of 1:1, with ratios of 9:1 and 3:1 showing improved activity than that of the palladium catalyst alone. This project is part of a larger effort to develop an effective, low-cost, platinum-free cathode catalyst for PEFC technologies. Future work will include a broader characterization of the palladium-based bimetallic catalyst for practical use in a PEFC, along with the study of other palladium-based bimetallic systems.

**In-Situ Analysis of Platinum Degradation for Fuel Cell Catalysts Using Small-Angle X-Ray Scattering.** JAMES GILBERT (University of Illinois at Chicago, Chicago, IL); MATT SMITH (Argonne National Laboratory, Argonne, IL). Catalyst durability during Polymer Electrolyte Fuel Cell (PEFC) operation remains a key challenge in developing a cost effective PEFC with an acceptable lifetime for both automotive and stationary power generation. Understanding the mechanisms of catalyst degradation is essential for furthering research toward lengthening fuel cell lifetimes. Platinum (Pt) and platinum-alloys are considered to be state-of-the-art catalysts for PEFCs. The precise method of the Pt corrosion is still unknown. However, several mechanisms have been proposed such as Pt dissolution and re-deposition (Ostwald ripening), coalescence of platinum particles via migration on the carbon support, and Pt particle agglomeration triggered by corrosion of the carbon support. Novel synthesis of nano-sized catalyst particles has improved power performance and lowered material cost. However, it is observed that the smaller the particles the faster the degradation and agglomeration via, nominally, the above mechanisms. Small Angle X-Ray Scattering (SAXS) is a powerfully accurate X-ray technique for characterizing particle size, especially between 1 and 100 nm. Thus SAXS is highly specific to the nano-sized Pt catalysts, which have been observed to aggregate to as much as 30 nm from an initial size of approximately 2–3 nm. In this study, samples of 20 wt% (2.2 nm) and 40 wt% (2.8 nm) Pt supported on commercial Vulcan XC-72 carbon were characterized *in-situ* using SAXS while cycling the potential between 0.4 and 1.4 V for up to 16 hours in an electrochemical half-cell. Particle size change was observed to increase 55% and 50% for the 20 wt% and 40 wt% Pt/C catalysts, respectively. SAXS data shows trends in particle growth correlated to cycle time and electrochemical potential. The results contained in this study have significant implications with regards to the durability of carbon-supported Pt-based nano-sized catalysts. These results also make a significant contribution to the larger effort in determining the mechanism by which Pt degrades.

**Separation of Lanthanide Ions with Kläui Ligand Resin.** TRINITY GRANGER (University of the Virgin Islands, St. Thomas, VI); GREGG LUMETTA (Pacific Northwest National Laboratory, Richland, WA);



VICTORIA HENRY (University of the Virgin Islands, St. Thomas, VI). Separation and pre-concentration of the desired analyte is often a critical step in many radioanalytical methods. Current procedures for separating and concentrating analytes for detection are complex, and can be both expensive and time consuming. Therefore, the purpose of this research is to develop an alternative method of separating lanthanide ions through the use of an extraction chromatography resin containing a Kläui ligand salt. This research is a continuation of a concerted effort to develop new methods of detecting small concentrations of radionuclides and lanthanides using Kläui ligands. The Kläui ligands,  $C_5Me_5Co(OP(OR)_2)_3$  (R=Me, Et, i-Pr, n-Pr) ( $L_{OR-}$ ), have unique affinity for lanthanide and actinide ions in the presence of competing metal ions. The use of 1 wt%  $NaL_{OR}$  (R=Et or n-Pr) adsorbed onto resin support has been shown to extract lanthanide ions from aqueous nitric acid solutions of different concentrations. In order to further evaluate the utility of these materials in radiochemical separation, the selectivity of the resins for the different lanthanide ions was examined by measuring the distribution coefficients ( $K_d$ ) for a series of lanthanide over a range of solution conditions. Based on prior research with actinide ions, it was hypothesized that the lanthanide ions would bond strongly with the Kläui ligands. The success of this research is important, because it will assist in expanding and improving current automated radiochemical methods, which will decrease the cost of developing and implementing radiochemical methods. To date,  $K_d$  values have been determined for  $Eu^{+3}$ ,  $Nd^{+3}$  and  $Pr^{+3}$  under varying nitric acid ( $HNO_3$ ) concentration, using a resin consisting of 1.0 wt%  $NaLOPr$  on Amberlite XAD-7HP. The dependence of the  $K_d$  values for  $Eu^{+3}$  has also been examined as a function of the ligand-to-europium ratio and the nitrate concentration. Decreasing  $K_d$  values were obtained upon increasing the nitric acid concentration, indicating protonation of the ligand, which competes with binding of the lanthanide ions. As expected, increasing the Kläui ligand-to-europium ratio results in increasing  $K_d$ , but no conclusions could be made from these data regarding stoichiometry of the complex formed on the resin. No dependence of the  $K_d$  on the nitrate concentration was observed, supporting the notion that the  $HNO_3$  dependence is dominated by the presence of the acidic hydronium ion (as opposed to the nitrate ion). Future work will involve the determination of the  $K_d$  values for the remainder of the lanthanide series to further assess the potential of the Kläui ligand for intra-group lanthanide separations.

**Synthesis of Ionic Liquids for Toxicity Studies.** JINHEE GWON (CUNY Queensborough Community College, Bayside, NY); JAMES F. WISHART (Brookhaven National Laboratory, Upton, NY); XING LI (Queensborough Community College, New York, NY). Ionic liquids (ILs) have potential uses as green solvent alternatives due to their relative non-volatility, non-flammability, wide liquid range, and high conductivity when compared to volatile organic solvents. Understanding the possible IL toxic effects on the environment before replacing the current solvents with them is critical. Reports suggest that many ILs are toxic to organisms varying from nematodes to algae and fish. However, those studies do not indicate a relationship between the purity of the ILs and their toxic effects. This investigation explores that relationship. A series of halide salts based on N-methylpyrrolidine were successfully prepared. N-methylpyrrolidine was reacted with alkyl halides of various chain lengths to produce the corresponding quaternary ammonium halide salts. These alkyl halides include 1-Bromobutane, 1-Bromopentane, 1-Bromodecane, 1-Bromododecane, and 1-Bromooctadecane. The quaternary ammonium halide salts were purified by washing with ethylacetate and diethylether. The structures of the salts were confirmed using H-1 and C-13 Nuclear Magnetic Resonance (NMR) spectroscopy. The salts were then converted to ionic liquids bearing the phosphate ( $PO_4^{3-}$ ) and bis(trifluoromethylsulfonate) ( $NTf_2^-$ ) anions. These liquids were prepared in different levels of purities. Purity was checked using NMR, fluorescence and UV-visible absorbance spectroscopy. This is a part of a larger collaborative research project where other similar series of ionic liquids based on imidazolium and pyridinium cations were prepared and screened for their toxicity to a variety of microorganisms.

**Dynamic Dissolution Testing of Nanoporous Niobium Phosphate.** KATHERINE HARRIS (The College of William and Mary, Williamsburg, VA); DAWN WELLMAN (Pacific Northwest National Laboratory, Richland, WA). Leaks in storage tanks holding radioactive waste on the Hanford Site and other Department of Energy (DOE) sites have led to a need for *in situ* soil and groundwater remediation techniques. Nanoporous transition metal phosphates have been shown to be effective in reductively sequestering radionuclides, but their stability within subsurface conditions has not been evaluated. A conservative estimate of the stability of nanoporous niobium phosphate (NP-NbPO)

was quantified using single-pass flow-through (SPFT) dissolution testing under the pH range of 6–9 at 90°C. The tests were run until a steady-state rate of dissolution was reached. Inductively coupled plasma-optical emission spectroscopy (ICP-OES) analysis of effluent samples indicates that at 90°C the dissolution rate of NP-NbPO,  $4.31 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1}$ , is independent of pH. The high, pH-independent stability of NP-NbPO suggests it may serve as a stable, highly effective radionuclide barrier within the subsurface environment. Further quantification of dissolution rates under the temperature range of 5° to 60°C and evaluation of the migration of NP-NbPO through the vadose zone is pending. However, preliminary results show that NP-NbPO is a promising candidate for *in situ* remediation for radionuclide-contaminated soil and groundwater.

**\*Comparing the properties of pyridinium and 4-dimethylamino-pyridinium ionic liquids.** JASMINE HATCHER (Queens College, Queens, NY); JAMES WISHART (Brookhaven National Laboratory, Upton, NY). Ionic liquids, organic salts that melt below 100°C, are generally composed of a large organic cation and a relatively small inorganic anion. They have generated much interest due to their potential as alternative reaction media for a variety of applications including use in batteries, fuel cells, and for the storage and processing of nuclear waste. Ionic liquids can be designed to incorporate specific functionalities for certain uses ("task-specific ionic liquids"). The physical characterization and properties of 4 dimethylaminopyridinium (DMAP) based ionic liquids with varying functionalities in comparison to their pyridinium (py) analogues are reported here. In addition, this study examines the effect of the dimethylamino group of DMAP on the physical properties of these two series of ionic liquids. The dimethylamino group of DMAP is known to have catalytic properties and DMAP based ionic liquids are expected to have similar properties. The DMAP and pyridinium salts were synthesized using various alkylating agents such as 3-chloropropanol and 2-bromoethyl ethyl ether. The resultant halide salts were converted to ionic liquids bearing bis(triflyl)imide anion. Physical properties investigated include: viscosity, conductivity, and thermal profile. Preliminary results indicate that for both the DMAP and py systems, the ionic liquids containing alkyl groups have lower viscosities and higher conductivities at room temperature compared to those bearing hydroxyl groups. Results also suggest the presence of the dimethyl amino group on the pyridine ring has minimal effect on the conductivity and viscosity. The Butyl DMAP and Butyl Pyridinium ionic liquids had almost the same conductivity (2.12 mS/cm and 2.22 mS/cm respectively) and viscosity (9.950 cP and 9.122 cP at 850°C respectively). Future work will focus on the effect of the position of the dimethylamino group on the pyridine ring on the same properties.

**A study of Nitrogen-containing complexes of Zinc(II) as photocatalysts in the production of hydrogen peroxide.** JENNIFER HAYES (University of Wyoming, Laramie, WY); ROBERT DISSELKAMP (Pacific Northwest National Laboratory, Richland, WA). Hydrogen peroxide is a valuable chemical commodity and its use as a clean, easily stored, and high energy density fuel source may gain acceptance should there be efficient and sustainable methods of production from dioxygen and water using solar irradiation. The current method of manufacturing is not cost efficient and photocatalytic production from solar light is one approach that has not been explored in detail. The concentration of hydrogen peroxide produced in an ultraviolet (UV) irradiated environment using nitrogen-containing complexes of zinc(II) as photocatalysts was studied using isomers of imidazole, indazole, pyrazole, pyrazine, and phenylenediamine complexes. Three variables are at play in determining production efficiency including catalyst UV absorbance, photon output, and quantum yield. UV wavelengths between 280nm and 360nm were attained from a UV-B lamp. Sample catalyst complexes were immersed in water, aerated, and irradiated over time to initiate a redox reaction between dissolved oxygen and water using photoinduced ionization properties of the semiconductor system for electron transport. Concentration of at certain time intervals was determined by titration with potassium permanganate. Ultra-violet absorbance and percent transmittance of the photocatalyst solids were measured with a UV-VIS scanning spectrophotometer. Irradiation of multiple zinc complexes revealed Zn-5-amino indazole to have the greatest first day production of 62.63mM, 37% quantum yield for the first 24 hours. Para-phenylenediamine showed the greatest long-term production as concentrations increased for 70 hours before a decrease was measured. Isomeric forms of the catalyst's organic components did have an effect on production. Irradiation of diaminopyridine isomers indicated 2,3 and 3,4 structures were the most productive, each generating 32mM hydrogen peroxide. However, the 2,5 isomer showed no production. After 90 hours, significant decrease in was noticed in all samples, suggesting a stoichiometric rather than catalytic relationship.

In this study, Zn-indazole and certain isomers of Zn-diaminopyridine complexes seemed to be the most active among those tested, exhibiting greater production efficiency and producing the highest quantum yield based on UV-absorbance. Photocatalytic production of hydrogen peroxide using these compounds has a strong potential to be an energy and cost efficient prospect in a renewable energy economy.

**Synthesis of Novel Anion Receptors for Separation.** *TRINA HAYES, BETHTRICE THOMPSON, KIMBERLY TUCKER (Jackson State University, Jackson, MS); BRUCE MOYER (Oak Ridge National Laboratory, Oak Ridge, TN).* Synthesis of Novel Anion Receptors for Separations Bethtrice Thompson, Trina Hayes, Kimberly Tucker, Alamgir Hossian Jackson State University, Jackson, MS FAST Bruce Moyer, Peter Bonnesen Chemical Science Division Oak Ridge National Laboratory Many anionic species have become a major environmental and health concern. For example nitrate is an agricultural contaminant in soil and is also present in large quantities of radioactive waste. As for the health concern, nitrate that is above the U.S. Environmental Protection Agency's regulated contamination level in ground water has caused an increase in bladder cancer in women. These major concerns have led researchers to develop anions receptors that can detect, bind, separate, and remove anions from the environment. To address such needs, we have been carrying out the synthesis of monofunctional, difunctional, and trifunctional thiourea compounds and their guanidinium derivatives. We followed a multi-step synthesis in which our starting compounds are isothiocyanate and amine which are converted to the desired thioureas followed by methylation and aminolysis to afford the guanidinium derivatives. Making and breaking covalent bonds is applied to construct desired molecules. The new compounds are analyzed by NMR spectrometry. It is planned to obtain crystals from the compounds in order to determine their molecular structures by X-ray Crystallography. These receptors will be used for binding and separation of the target ionic species in complex mixtures. Binding properties of synthesized molecules for anions will be tested in different solvents using NMR spectrometry. This study will provide ground work for future cleanup and vitrification of USDOE wastes and environment streams.

**Determining the Extent of Delocalization in Mixed-Valence Iron Dimers Using X-ray Absorption Spectroscopy.** *ALISON HOYT (Yale University, New Haven, CT); KELLY GAFFNEY (Stanford Linear Accelerator Center, Stanford, CA).* This study examines the extent of charge delocalization in mixed valence compounds. Understanding the structure of charge delocalization is the first step in understanding the local dynamics of charge transfer. This insight has diverse applications such as the ability to mimic biological reactions and to enhance solar technology. Because of its fast time scale, synchrotron radiation was used to probe the iron K-edge for three organometallic systems. In these complexes, two bridged metal atoms share an effective charge of 5+. In a Robin-Day Class II compound, charge is localized and the two iron atoms have effective oxidation states of 2+ and 3+ respectively. For Class III delocalized compounds each metal center has an effective charge of 2.5+. Class II/III compounds exhibit characteristics of both localized and delocalized systems according to various optical spectroscopies. Synchrotron radiation was used to study charge distribution in these poorly-understood Class II/III intermediate systems. In the limit of absolute localization, spectra of the mixed valence species were expected to be a linear combination of the reduced and oxidized species. For the delocalized case, a linear combination was not expected. These two cases were used as calibration limits to determine the extent of delocalization in the unknown Class II/III compound. Results showed that synchrotron radiation classifies the Class II/III compound as localized. However, data also demonstrated that the linear combination model did not hold as expected and a revised model is necessary to better understand this phenomenon.

**Investigating the microwave-assisted synthesis of ionic liquids.** *KIJANA KERR (Queensborough Community College, Bayside, NY); JAMES F. WISHART (Brookhaven National Laboratory, Upton, NY).* Ionic liquids (ILs), which have gained a lot of attention as alternative solvents recently and have found industrial applications, are salts that are liquid at or near room temperature. This makes them good solvents for a range of organic and polymeric compounds. ILs typically consist of large nitrogen-containing organic cations and small inorganic anions. The need is increasing for developing synthetic procedures that are faster, more efficient, and more economical as the number of applications for ionic liquids increase. Typical advantages of microwave-assisted syntheses are to significantly reduce reaction times and increase the product yield. The microwave assisted syntheses of halide salts based on DABCO diazabicyclo[2.2.2]octane and their conversion into ionic liquids are reported here. Reaction conditions, such as the temperature, the nature of the reaction solvent and the

length of reaction time, have been varied. A comparison of these two synthetic techniques (thermal and microwave-assisted) and the physical characterization of these compounds are reported. Preliminary results show that quaternization has been achieved to produce mono- and di- substituted DABCO halide salts with different substituent groups such as alkyl, ethoxy and hydroxyl. Conditions have been worked out to obtain some of these salts in high yields, particularly alkyl containing DABCO salts. Structure determination of the resulting ionic liquids was done using <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR spectroscopy. Subsequent characterization, including differential scanning calorimetry (DSC), of a series of compounds is reported. Dramatic differences in melting points were observed with anion variation of DABCO compounds.

**The Characterization of Gadolinium-Loaded Liquid Scintillator: An Antineutrino Detector for  $\sigma_{13}$  Measurement.** *TIGISTI KESETE, IKENNA OKAFOR (Central State University, Wilberforce, OH); SELEEM, RICHARD HAHN, MINFANG YEH (Brookhaven National Laboratory, Upton, NY).* After the Sudbury Neutrino Observatory successfully observed three neutrino flavors and solved the 40-year-old solar neutrino problem, most of the neutrino experiments have been focusing on the understanding of the neutrino oscillation mechanism. Continued growth in this field depends strongly on the unknown mixing angle  $\sigma_{13}$ , a fundamental neutrino parameter that is needed as an indicative guideline for next-generation neutrino experiments. The Daya Bay collaboration proposed by scientists from U.S., China, and Russia are favored for  $\sigma_{13}$  measurement because their derivations for  $\sigma_{13}$  are relatively clean and unambiguous. The gadolinium-loaded liquid scintillator (Gd-LS) is the centerpiece of the antineutrino detector, and its key required characteristics are long-term chemical stability, long attenuation length, and high photon production. Research has indicated that three carboxylic acids-3,5,5-trimethylhexanoic acid (TMHA), 2-ethylhexanoic acid (EHA), and methylvaleric acid (MVA)-could interact with inorganic Gd aqueous solution to form organometallic carboxylate that could be extracted into the organic liquid scintillator by solvent-solvent extraction. However, the Gd-LS synthesized with these acids showed different chemical properties. To characterize their effects on the antineutrino detector, this summer research focused on: (1) purifications of TMHA, EHA, and MVA to improve their optical transparencies and chemical stabilities and determination of their dissociation constants (pKa) to better understand the chemical properties of the synthesized Gd-LS, and (2) comparisons of the phosphorescence and fluorescence effects to the photon production of Gd-LS with the carboxylic acids. Experimentally, vacuum distillation was used to purify the acids, and their purification effects were monitored using Shimadzu UV-1601 absorption spectrometer by the absorbance at 430 nm. Results indicated that the attenuation lengths for TMHA, EHA, and MVA were improved from 2.7 m, 1.6 m, and 1.8 m to 7.2 m, 6.2 m, and 10.9 m, respectively. The acid-base titrations for three acids were conducted with Accumet AR25 dual-channel pH/Ion meter by fitting their differential curves (Gaussian distribution), and their pKa values were determined to be below 5. For phosphorescence and fluorescence comparisons, the light-yield data indicated that the photon production of the Gd-LS was mainly dominated by fluorescence process. The characteristics of Gd-LS synthesized with these acids are still under further analysis.

**Electrochemical Remediation of Arsenic Contaminated Groundwater.** *KRISTIN KOWOLIK (University of California – Berkeley, Berkeley, CA); ASHOK GADGIL (Lawrence Berkeley National Laboratory, Berkeley, CA).* Millions of people worldwide do not have access to clean water. This problem is especially severe in Bangladesh where water is severely contaminated with arsenic. Chronic arsenic exposure has devastating health effects: cardiovascular diseases, cancers, and eventually death. Many methods of arsenic removal have been studied but most of these are too expensive and impractical to be implemented in poor countries such as Bangladesh. This project investigates electrochemistry as an affordable means of removing arsenic. Experiments are performed using a whisk like device made out of iron as the cathode and copper as the anode. Both electrodes are immersed in simulated groundwater spiked with an arsenic concentration of 600 ppb. During voltage application, currents of 70 mA and 110 mA are passed through the system. The water is stirred gently to ensure uniform electron distribution. While the electrochemical process is progressing, iron metal is oxidized to Fe(III). As an ionic species, iron will bind free arsenic in solution. After the desired amount of charge is passed, the treated water is allowed to precipitate for 24 hours and is then filtered by means of vacuum filtration. One of the significant major tasks of the project was to develop an experimental protocol (methods, measurement techniques, experimental conditions) to obtain proof of concept, so this process can be investigated further.



We showed that if certain conditions are met such as (1) optimal charge per volume, (2) optimal current density and (3) precipitation time of 24 hours, promising results are obtained. An initial arsenic concentration of 600 ppb can be reduced to a final concentration of 50 ppb in 2.5 L water by application of 70.08 C/L at 70 mA and 107.5 C/L at 110 mA. These results are very encouraging and provide great promise that electrochemistry is a powerful, and most importantly, an affordable tool in the remediation of arsenic from contaminated groundwater.

**Integrated Electrodialysis Membrane Process for Beneficial Use of Coalbed Methane Produced Water.** *STEPHANIE LE CLAIR (Saint Mary's College of California, Moraga, CA); PAULA MOON (Argonne National Laboratory, Argonne, IL).* During oil and gas production, the water that is trapped in underground formations is brought to the surface. About 15–20 billion bbl of this water, known as produced water, is generated in the United States each year. The Colorado Energy Research Institute at the Colorado School of Mines has brought together a team of scientists and engineers to address produced water management. In support of this effort, Gas Technology Institute and Argonne National Laboratory have been collaborating in using electrodialysis (ED) to remove ions from water in the Powder River Basin (PRB) so that the water may be used for irrigation or livestock drinking water. In most states, the criteria needed for beneficial use include averages of total dissolved solids of 1,000–2,000 mg/L, a pH range of 6–8, and a sodium absorption ratio (SAR) of less than 6. In order to meet water discharge specifications, experiments were conducted with produced water from the PRB area to determine the parameters needed for the ED system. The electrodialysis membrane type, current density, stock concentrations, and power consumption were tested to find an optimum for each variable. Different post-demineralization treatments were also performed, using calcium carbonate, calcium sulfate and limestone, to determine which was the most effective at desalting the water, after the use of the ED system. Results showed that the best configuration for the ED system consisted of using of a non-selective membrane as the cation membrane, a sodium bicarbonate solution as the concentrate and a current density of 4.00 mAmps/cm<sup>2</sup>. This setup provided the most cost-effective ED system, yielding 88.9% desalination with a modest energy input of 0.18 kWh/lb of NaCl removed. For post-treatment demineralization, limestone proved to be the most cost-effective way to lower the SAR value to below 6. These experiments showed that it should be possible to desalt the produced water up to around 80% and then treat the water with limestone to reach the water quality needed to dispose of it for beneficial use. A long term membrane stability experiment is currently underway.

**Separating and Recovering Materials from Shredder Residue.** *STEPHANIE LE CLAIR (Saint Mary's College of California, Moraga, CA); JOSEPH POMYKALA, JR. (Argonne National Laboratory, Argonne, IL).* Every year, 4.5 million metric tons of shredder residue — a complex heterogeneous mixture generated from shredding automobiles, electrical appliances, construction debris, and other metal-containing materials — is landfilled. Argonne National Laboratory has been developing a mechanical process to separate and recover various materials from shredder residue. The process has successfully recovered ferrous metals, nonferrous metals, a mixture of polypropylene and polyethylene, and acrylonitrile butadiene styrene. Byproducts from this process include two fractions, referred to as fines, that are on average 40% by weight of the starting shredder residue. One objective of the project was to determine the technical feasibility of separating and recovering polymers and metals from the fines. Analysis was conducted on samples from a 100 pounds experiment to complete a mass balance and determine the quantities of recoverable materials of value, such as plastics, rubber compounds and metals. The tests showed that it was technically feasible to separate and recover from the fines a polymer concentrate fraction, which accounted for 19.1% by weight of the starting shredder residue. This fraction contained 9.9 wt.% metals, 18.3 wt.% plastics, 54.5 wt.% rubber, and 17.3 wt.% others, including rocks, fibers, and foams. Future work will involve developing a method to separate and recover the metals from the polymer concentrate fraction. The plastics will then be processed through the Argonne developed froth-flotation process. Another objective of the project was to determine what cleaning processes would be more successful in removing the polychlorinated biphenyls (PCBs) from the plastics. For any product recovered from shredder residue to be reintroduced into the U.S. market, it must contain a PCB concentration of less than 2 ppm. Current commercial methods to remove PCBs to below this limit are not cost effective. Benchscale tests were conducted by using washing solutions with different catalysts, two different solvents, and various thermal desorption techniques. The

plastic samples were then sent to Environmental Monitoring Technology for analysis. The received analytical results showed that none of the methods were able to remove the PCBs to a concentration below 2 ppm. The analytical results for all of the experiments have not been received yet, however. Future work will involve larger scale testing of the most promising approach.

**Evaluation of relative metal nucleophilicities of diphenyldithiophosphinate ligands Using gas-phase dissociation reactions.** *CHRISTOPHER LEAVITT (Wichita State University, Wichita, KS); ANITA GIANOTTO (Idaho National Laboratory, Idaho Falls, ID).* The relative metal cation nucleophilicities of a series of unique diphenyldithiophosphinate ligands were evaluated by forming [metal-mixed ligand]- complexes, then fragmenting them using competitive collision induced dissociation. The bis(trifluoromethyl phenyl)dithiophosphinate anions are of high interest because they have demonstrated potential for exceptional separation of Am<sup>3+</sup> from lanthanide trications. With respect to sodium and europium (III), the unmodified diphenyldithiophosphinate anion (Lu-) was compared with three different ligands, which varied in terms of the position of the trifluoromethyl (TFM) group on the phenyl rings: bis(ortho-TFM) (L1-), (ortho-TFM)(meta-TFM) (L2-), and bis(meta-TFM) (L3-). Relative to Na<sup>+</sup>, the unmodified Lu- anion was the strongest nucleophile. Comparing the TFM derivatives, the bis(ortho-TFM) derivative, L1-, was found to be the strongest nucleophile, while the bis(meta-TFM), L3-, was the weakest, and the mixed ortho,meta derivative was intermediate. Similar experiments were performed using europium nitrate complexes; ionic dissociation of these complexes always produced the anionic TFM ligands, showing again that the unmodified Lu- was the strongest nucleophile. The europium (III) nitrate complexes also underwent redox elimination of radical ligands. The tendency of the ligands to undergo oxidation and be eliminated as neutral radicals followed the same trend as the nucleophilicities for Na<sup>+</sup>, viz. Lu- > L1- > L2- > L3-.

**Determination of Silica in Uranium Casting Pins Samples by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES).** *MEGAN LONGO (Albertson College of Idaho, Caldwell, ID); JEFFREY GIGLIO (Idaho National Laboratory, Idaho Falls, ID).* An analytical method was developed for the determination of Silica (Si) in Uranium casting pins. The new method utilized an Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES) for the determination of Si at 250.69 nm and 251.611 nm. The Si lines yielded instrument detection limits (3s) of 0.007 and 0.02 µg/mL, respectively. The method detection limits for the new analytical method are 50 µg/g in the solid. An interfering element correction had to be employed because of a spectral interference from U. The U concentration in the solutions analyzed by ICP-AES was approximately 1150 µg/mL. Spiked sample recoveries yielded complete recoveries, within the experimental error of the analysis. The new ICP-AES method was compared to a molybdenum blue colorimetric method. Results were comparable, within the experimental error of both measurements.

**Varying Parameters to Increase DNA Encapsulation in Biodegradable Nanospheres for Drug Delivery Applications.** *TRACEY MAMMA (Norfolk State University, Norfolk, VA); CAROL J. MERTZ (Argonne National Laboratory, Argonne, IL).* Nanoparticles are submicron-sized polymeric colloidal particles that can have a therapeutic agent of interest encapsulated within, conjugated on the surface or absorbed on the surface of their polymeric matrix. In recent years, biodegradable nanospheres have become the focus of extensive research. We will evaluate the use of various solvents (primarily dichloromethane, acetone, and chloroform), in combination with different molecular weights of PLGA, to determine the most effective combination to produce high DNA encapsulation and minimal particle size. For biomedical applications these nanospheres are made of biodegradable and biocompatible polymers of poly (D, L-lactide-co-glycolide) (PLGA) and allow controlled and protected delivery of a therapeutic agent encapsulated in the polymer core. Research on the use of these polymers has shown a wide range of encapsulation efficiencies for DNA when a double emulsion (w1/o/w2) method was used. In this study, the focus is on increasing the encapsulating efficiency of DNA into biodegradable/biocompatible nanospheres for drug delivery application. When FDA approved materials are used in the manufacturing of the nanoparticles, the laboratory and animal testing phase may be shortened allowing the nanospheres to move to the human clinical trials sooner. While varying the synthesis parameters, the goal is to optimize the encapsulation of DNA while tailoring the size of the nanospheres. These particles can be tailored to target specific cellular/tissue, improve oral bioavailability, solubilize drugs for intravascular delivery, solubilize drugs for and improve the

stability of the therapeutic agents, specifically against enzymatic degradation (nucleases and proteases).

**Power Density and Longevity of Solid Oxide Fuel Cells.** AMANDA MANLEY (College of Dupage, Glen Ellyn, IL); RICHARD JARMAN (Argonne National Laboratory, Argonne, IL). The solid oxide fuel cell (SOFCs) are an electrochemical energy conversion device. The objective of this project is to improve the power density of a solid oxide fuel cell while using components that are lower in cost and have more chemical and physical durability. Tri-layer cells were made by tape casting. They consisted of a hydrogen electrode, an electrolyte, and a porous stainless steel support layer. This design increases the stability of the hydrogen electrode while allowing more flexibility in sintering options than traditional ceramic supported SOFC, while at the same time reducing the cost of the fuel cell. The tri-layer cell was evaluated using the scanning electron microscope to determine the distribution of elements after sintering. The oxygen electrode was screen printed onto a previously sintered tri-layered cell which was then sintered again. One of the objectives was to find the optimal sintering temperature for the oxygen electrode, to minimize the potential for oxidation of the stainless steel support. The power density characteristics of the device were then measured using electro-chemical impedance spectroscopy, and cell DC polarization. By increasing the power density of SOFCs that run at a lower operating temperature they may be more widely utilized for a broader selection of applications.

**Determining the Local Structure of Platinum Streptidine Using X-Ray Absorption Spectroscopy.** MICHAELLE MAYALU (Massachusetts Institute of Technology, Cambridge, MA); SERENA DEBEER GEORGE (Stanford Linear Accelerator Center, Stanford, CA). X-Ray absorption spectroscopy (XAS) is a technique that utilizes high energy X-rays commonly obtained from synchrotron radiation to determine the structure of known and unknown substances and materials. By examining the absorption vs. energy pattern, one can determine the local structure surrounding the absorbing atom. Analysis of a region of the absorption vs. energy graph called extended X-ray absorption fine structure (EXAFS) leads to information about the identity of the atoms surrounding the absorber, the number of atoms surrounding the absorber, and the distances between the absorber and neighboring atoms. Using XAS, structural descriptions of platinum streptidine, a newly synthesized platinum anti-cancer agent, have been obtained. The results show that the platinum is in fact coordinated to the streptidine, which was the main question that needed to be answered about the drug.

**\*Developing a Single Source Precursor for Next Generation Lithium Ion Batteries.** TONI MCINTYRE (Fayetteville State University, Fayetteville, NC); JONATHAN BREITZER (Argonne National Laboratory, Argonne, IL). The electrical conductivity of manganese oxides make them an ideal cathode material in lithium ion batteries. Coupled with the electrochemical stability of titanium, this combination proved to be an excellent cathode with exceptional electrochemical performance. Using a single source precursor method for combining these ions demonstrated a much better performing cathode material than by physically mixing them, due to the resulting smaller crystal size and better cation mixing. The precursor  $\text{MnTiO}(\text{C}_2\text{O}_4)_2$  was synthesized by first forming a stable solution of  $\text{H}_2\text{TiO}(\text{C}_2\text{O}_4)_2$ , and then adding a stoichiometric amount of Mn(II) to precipitate the final product.  $\text{LiOH} \cdot \text{H}_2\text{O}$  was added and the sample was heated to  $300^\circ\text{C}$  to produce the desired material,  $\text{Li}_2\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_3$ .  $\text{Li}_2\text{Ni}_{0.5}\text{Ti}_{0.5}\text{O}_3$  can also be synthesized using this method. The ceramic sample was formed by physically grinding  $\text{MnO}$ ,  $\text{TiO}_2$ , and  $\text{LiOH} \cdot \text{H}_2\text{O}$  and heating in air at  $900^\circ\text{C}$ . The ratio of Ti to Mn was varied by synthesizing a precursor with Ti and  $\text{H}_2\text{C}_6\text{H}_{12}\text{N}_2$  (DABCO) replacing Mn as the +2 cation. Coin cells were constructed using four different materials as the cathode laminates, lithium metal as the anode, and 1.2M  $\text{LiPF}_6$  in a 3:7 %wt mixture of ethylene carbonate (EC)/diethyl carbonate (DEC) as the electrolyte. The coin cells were tested by cycling them from 4.85 V to 1.8 V with a fixed current of 0.16 mA at room temperature. The cells containing the laminates prepared using the precursor method with a 1:1 metal ratio performed better than the other batteries, with an average first cycle capacity of 350 mA-h/g. The laminates with the 2:1 (Ti to Mn) ratio had an average first cycle capacity of about 100 mA-h/g, but had a very stable cycle pattern. The physically synthesized laminate had an average first cycle capacity of about 50 mA-h/g. The compound containing only Ti had a first cycle capacity of about 0.03 mA-h/g. The precursor method of synthesizing these cathode materials proved to be more electrochemically favorable than the ceramic method. Further studies on increasing the ratio of manganese to titanium may further optimize the electrochemical performance of cathodes.

**\*Analysis of Some Near-Infrared Spectra of  $\text{C}_2\text{Br}$ .** ELIZABETH MILLINGS (Suffolk County Community College, Selden, NY); TREVOR SEARS (Brookhaven National Laboratory, Upton, NY). In combustion chemistry, the  $\text{C}_2\text{H}$  molecule has been studied extensively because it is an important intermediate and provides an example of the breakdown of the Born-Oppenheimer approximation. A related molecule,  $\text{C}_2\text{Br}$ , supplies a different view of the Born-Oppenheimer breakdown, and its rotational, vibrational, and electronic structure can be compared to  $\text{C}_2\text{H}$ . Previously, only computational studies have been reported regarding  $\text{C}_2\text{Br}$ . Its energy states and spectra were theoretically determined, and a model equation was developed to describe its rotational energy levels. Recently, a spectrum of  $\text{C}_2\text{Br}$  was accidentally detected at Brookhaven National Laboratory, and a portion of it was tentatively assigned to some P-branch rotational transitions. In this project, the spectroscopic data were further examined in an attempt to confirm the assignments, determine the rotational constants, identify spectral lines corresponding to the two bromine isotopes, and identify the band origins. To accomplish this, a LabVIEW computer program was developed and used to calculate the energy levels and predict spectra, which were then compared to the experimental near-infrared (NIR) spectra. The error between the data and the calculations was minimized by adjusting the modeling constants and testing possible assignments. A simulated spectrum was created with each new calculation enabling a set of "best fit" values to be determined. This analysis is part of a larger work investigating the chemical processes of combustion by studying the structure and dynamics of intermediate reactive species.

**Novel Reduction of Monosaccharides and Disaccharides using Palladium-Carbon Catalysts.** FIONA MILLS-GRONINGER (Manchester College, North Manchester, IN); GEORGE KRAUS (Ames Laboratory, Ames, IA). Mixtures of sugars as by-products of industrial processes are difficult and expensive to separate. This will be increasingly important in the emerging cellulose ethanol industry in which large volumes of carbohydrates will be produced. By reducing the different sugars in a mixture to a single product in a single-step reaction, the resulting carbohydrate can be easily used in further processes. Reductions of carbohydrates using palladium-catalyzed reactions are documented in literature, typically with lengthy reaction times. In this study, mono- and disaccharides are reduced using a novel combination of palladium-carbon catalyst, formic acid, and concentrated sulfuric acid heated to  $80^\circ\text{C}$ , producing the reduced form of the simple carbohydrate after one hour. Reaction progress was determined using 300 and 400 MHz proton NMR. After successful production of the reduced sugar, the compound was acetylated using acetic anhydride and purified using TLC and flash column separation. Various acetylation conditions were attempted, and reaction efficiency was determined using the NMR spectra as well as qualitative TLC comparison. Reduction was confirmed by comparing the spectra of the carbohydrate starting material with spectra after reduction. The spectra of a-methyl-D-glucopyranoside (methoxy glucose), dextrose, D-cellobiose, and sucrose showed distinct differences from the starting material indicative of reduction. Furthermore, comparison of the spectra of reduced forms of methoxy glucose, dextrose, and cellobiose showed almost identical peaks consistent with production of a single reduced product. The complex carbohydrate cellulose acetate was unable to be reduced using this method. Future work will include optimizing conditions for acetylation as well as determining conditions for effective reduction of complex carbohydrates.

**Determination of Naturally Occurring versus Process Introduced Beryllium at Lawrence Livermore National Laboratory.** JENNIFER MULLINS (Randolph-Macon Woman's College, Lynchburg, VA); RYAN KAMERZELL (Lawrence Livermore National Laboratory, Livermore, CA). The DOE Title 10 Code of Federal Regulations, Part 850, Chronic Beryllium Disease Prevention Program defines the maximum removable surface contamination of beryllium (Be) in non-Be work areas as the higher of  $0.2 \mu\text{g Be}/100\text{cm}^2$  or the concentration of Be in soil at the point of release. Be is a naturally occurring metal and can be found on surfaces in concentrations greater than the defined DOE release limit without a process present that would introduce contamination. Until now there has been no standardized method for deciphering between naturally occurring and process introduced Be. The purpose of this research was to develop such a method by determining naturally occurring ratios of Be to other naturally occurring metals in soil at Lawrence Livermore National Laboratory (LLNL). Sixty random soil samples were collected from uncontaminated locations within the LLNL site boundary. The samples were analyzed for the concentrations of Be and 19 other metals using an Inductively Coupled Plasma Spectrometer. Aluminum (Al), nickel (Ni), and vanadium (V) were selected to calculate the naturally occurring ratios based upon



detection rates, low variability, and R-values from the Ryan-Joiner W-test for normality. Two-sided 95% upper and lower tolerance limits (UTL and LTL) were calculated for the true 95th percentile of each naturally occurring ratio: [Be]:[Al]- UTL97.5%, 95% =  $5.06 \times 10^{-5}$ , LTL2.5%, 95% =  $4.35 \times 10^{-5}$ , mean =  $3.40 \times 10^{-5}$ ; [Be]:[Ni]- UTL97.5%, 95% =  $1.73 \times 10^{-2}$ , LTL2.5%, 95% =  $1.30 \times 10^{-2}$ , mean =  $8.12 \times 10^{-3}$ ; and [Be]:[V]- UTL97.5%, 95% =  $1.63 \times 10^{-2}$ , LTL2.5%, 95% =  $1.38 \times 10^{-2}$ , mean =  $1.05 \times 10^{-2}$ . Sample data suggests with 95% confidence that 95% of the ratios do not exceed the true UTL when beryllium is naturally occurring. Future data can be compared to the ratios to conclude the following: (1 if the sample ratio is less than the LTL, the Be is naturally occurring, (2 if the sample ratio is greater than the LTL but less than the UTL, further investigation is required, and (3 if the sample ratio is greater than the UTL, the Be is process introduced. Other DOE sites can use this method to determine their own ratios to discriminate between naturally occurring and process introduced Be. The ability to determine this will allow for redirection of resources away from unnecessarily implementing decontamination requirements for cleaning surfaces with false contamination. Implementing this method would be fiscally responsible while not increasing employee health risk.

**Simple Route to Control Nanoscale Domain Morphology in Block Copolymer Films.** ELIZABETH NETTLETON (*University of South Dakota, Vermillion, SD*); SETH DARLING (*Argonne National Laboratory, Argonne, IL*). As demand for increasingly smaller devices grows, new efficient patterning techniques must replace traditional lithographic methods. Self-assembly presents a possible technique by which to pattern materials using a parallel, bottom-up process. Gaining control over the structure and order of self-assembled domains is critical to the success of this methodology. This study focuses on the self-assembly of thin films of polystyrene-block-poly(ferrocenyldimethylsilane) block copolymers (PS-*b*-PFS) on silicon nitride substrates. Upon annealing, the thin films microphase separate to form nanoscale PFS cylinders within a PS matrix. Traditionally, order in such films is improved using thermal annealing, which has drawbacks including time requirements and the possibility for thermal degradation. In this work, solvent annealing, an alternative to thermal annealing, is used. By varying solvent anneal times, either in-plane or standing cylinder domains can be achieved. In order to characterize cylinder structures, reactive ion etching was used to remove the PS matrix and the remaining PFS cylinders were imaged via atomic force microscopy (AFM). Because of the comparatively high etch resistivity of the PFS block, this block copolymer holds potential in lithographic patterning of nanowires, nanopillar arrays, and nanofluidic channels.

**Development of Production and Purification Procedures for Calbindin D9k Mutants for Solid State Nuclear Magnetic Resonance Spectroscopy.** SHELLEY NI (*Stanford University, Stanford, CA*); ROBERT HECK (*Pacific Northwest National Laboratory, Richland, WA*). Calbindin, a metalloprotein with two calcium binding sites, is present in multiple species and involved in biological processes as varied as calcium transport in fruit fly neurons and mammalian intestinal calcium uptake. Despite its ubiquity, its biological roles, and binding behavior are unknown. This paper focuses on the preparation of 9 kDa calbindin for solid state nuclear magnetic resonance (ssNMR) spectroscopy. Our purified calbindin will be used for the first ssNMR experiments studying calcium within a protein. To best understand the structure and mechanisms of calbindin's binding sites, each site must be studied separately. To accomplish this, two calbindin mutants were to be prepared for ssNMR spectroscopy. Each mutant had been altered so that only one binding site retained its original structure and function. A synthetic gene was inserted into a pET expression system to produce calbindin mutants using *Escherichia coli*. After harvesting the cells, protein was purified primarily with ion exchange and gel filtration chromatography. However, several analyses using SDS-PAGE Tris-tricine and Tris-HCl gels made it evident that D9K P43M E65Q was not expressing well in *E. coli* BL21(DE3) or *E. coli* BL21(DE3) pLysS competent cells. Instead, we then purified calbindin D9K P43M, which had both binding sites intact. The ssNMR spectrum of a previously made calcium binding mutant E27Q P43M can be removed from that of calbindin D9K P43M, still allowing for study of the other calcium binding site. Though purification of the initial calbindin double mutant P43M E65Q was found unfeasible, a combination of earlier calbindin purification procedures were successfully adapted to purifying D9K P43M to homogeneity as determined by SDS-PAGE. With the aid of a fermentation unit, these methods should be easily scaled up to produce the required quantities needed for planned ssNMR experiments.

**Electronic Characterization of Rare Earth-Doped.** ANDREW OLSON (*Carleton College, Northfield, MN*); DALE L. PERRY (*Lawrence Berkeley National Laboratory, Berkeley, CA*). Zinc telluride and telluride-

containing compounds have been extensively analyzed by X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) in order to determine the chemical states and shifts in electronic energy levels of the elements present in the materials. To a lesser extent, chemical shifts of gadolinium lines in various compounds have also been studied. However, the characterization of ZnTe:Gd by XPS and AES is practically non-existent. Use of this material as a semiconductor in various applications requires that electrical contact be maintained between the material's surface and other electrical components. Buildup of oxides and other species on the surface can cause insulating effects, hampering the material's intended performance. It is, therefore, of interest to study surface reactions of the compound with air in order to identify surface product films that may adversely affect the utility of ZnTe:Gd as a multipurpose semiconductor. The current study was an initial characterization of these materials using XPS and AES. Observed spectra for the initial, "as received" surface yielded data consistent with the presence of  $\text{Gd}_2\text{O}_3$ , ZnO, and  $\text{TeO}_2$ . Spectral parameters including binding energies, spin-orbit splitting, satellite structure, and kinetic energy Auger lines of elements compared favorably to analogous features in spectra of other Zn-Te-Gd compounds. Surface charging of the material was observed and studied in conjunction with argon ion sputtering. The results indicated that insulating surface films do indeed form on these materials in air, films that can act as interfacial layers between the semiconductor material and other materials such as electrical contacts attached to the surface of the semiconductor. A future examination of this material by other characterizing methods and types of instrumentation will provide further insight into the chemistry, structure, and electronic properties of this material and shed more light on the formation of the surface layers under ambient air exposure.

**Inkjet Printing of Nickel and Silver Metal Solar Cell Contacts.** ROBERT PASQUARELLI (*Rochester Institute of Technology, Rochester, NY*); CALVIN CURTIS (*National Renewable Energy Laboratory, Golden, CO*). With about 125,000 terawatts of solar power striking the earth at any given moment, solar energy may be the only renewable energy resource with enough capacity to meet a major portion of our future energy needs. Thin-film technologies and solution deposition processes seek to reduce manufacturing costs in order to compete with conventionally coal-based electricity. Inkjet printing, as a derivative of the direct-write process, offers the potential for low-cost, materials-efficient deposition of the metals for photovoltaic contacts. Advances in contact metallizations are important because they can be employed on existing silicon technology and in future-generation devices. We report on the atmospheric, non-contact deposition of nickel (Ni) and silver (Ag) metal front contacts from metal-precursor organic inks on a Dimatix inkjet printer at 180–220°C. Near-bulk conductivity Ag contacts were successfully printed up to 4.5  $\mu\text{m}$  thick and less than 125  $\mu\text{m}$  wide on the silicon nitride antireflective coating of silicon solar cells. Thin, high-resolution Ni adhesion-layer lines were printed on glass and zinc oxide at 55 nm thick and 80  $\mu\text{m}$  wide with a conductivity two orders magnitude less than bulk. Additionally, the ability to print multi-layered metallizations (Ag on Ni) on transparent conducting oxides was demonstrated and is promising for contacts in copper-indium-diselenide (CIS) solar cells. Future work will focus on further improving resolution, printing full contacts on devices, and investigating copper inks as a low-cost replacement for Ag contacts.

**Optimal Mixed-Acid Digestion Procedures for Sediment and Tissue Using a Hot Block Heating System.** JULIA PETERSEN (*Western Washington University, Bellingham, WA*); GARY GILL (*Pacific Northwest National Laboratory, Richland, WA*). Investigations were conducted to optimize mixed-acid digestion procedures for sediments and tissues using a hot block heating system with disposable vials. This method is more cost efficient and less labor intensive than digestion methods using high pressure heating in sealed Teflon vessels. A series of digestions were conducted using varying procedures on several Standard Reference Materials (SRMs). The acid mixtures employed included, aqua regia (3:1 nitric: hydrochloric acid), aqua regia plus hydrogen peroxide and several combinations of hydrochloric/ nitric/ hydrofluoric/ boric acid patterned after the procedures used at Texas A&M University (TAMU) and for the National Status and Trends Program (National Oceanic and Atmospheric Association). The digestates were analyzed by Inductively Coupled Plasma-Optical Emission Spectrometry and percent recoveries were calculated from certified and reference values. Very few elements (Cu, Ag, and Cd) had acceptable recoveries (>90%) for the aqua regia and the aqua regia plus hydrogen peroxide digestion of sediments. The TAMU digestions showed an overall increased recovery of 7% for a collective group of 15 elements (Al, As, Ba, Be, Ca, Cu, Fe, K, Mg, Mn, Mo, Na, Sr, V and Zn)

when the procedure included a heating step after boric acid was added. Recoveries were >90% for the National Status and Trends procedures for the group of 15 elements which proved to be most comprehensive sediment method. This digestion included 2 mL  $\text{HNO}_3$ , 3 mL  $\text{HCl}$ , 2 mL  $\text{HF}$ , and 15 mL 5% boric acid with a heating step after  $\text{HCl}$ ,  $\text{HF}$  and boric acid were added. For the tissue digestions, the best recoveries were observed when the sample was allowed to sit overnight with only nitric acid added at room temperature before initiating a heated mixed-acid (2 mL  $\text{HNO}_3$ , 3 mL  $\text{HCl}$ , and 2 mL of  $\text{H}_2\text{O}_2$ ) digestion procedure the following day. Recoveries >90% were observed for the elements Ag, Ca, Cu, Fe, K, Mg, Mn, Na, Ni, Sr, and Zn. Further work could include the use of an Inductively Coupled Plasma-Mass Spectrometer to monitor additional elements as well as studying matrix effects on the difficulty of digestion.

**Protein-Assisted Magnetite Nanoparticle Synthesis.** TIMOTHY PICA (*University of California at Berkeley, Berkeley, CA*); TANYA PROZOROV (*Ames Laboratory, Ames, IA*). Uniform magnetite nanocrystals were synthesized in the presence of the biomineralization protein mms6 involved in the biomineralization of magnetite in bacterial magnetosomes. Several recombinant mms6 proteins were tested: polyhistidine-tagged full-length mms6 protein (his-mms6), a 25 amino acid segment from the C-terminus of this protein (c25-mms6), and a glutathione S-transferase enzyme-tagged mms6 protein (GST-mms6). The his-mms6 protein was reported to facilitate formation of ~30 nm, single-domain, uniform, isomorphous magnetite nanocrystals in aqueous polymeric gel, as verified by transmission electron microscopy analysis and magnetization measurements. Conjugating the proteins to activated Pluronic polymer allowed further control over particle growth. Similarly, the c25-mms6 protein was also shown to promote shape-selective formation of magnetite nanocrystals. Preliminary fast protein liquid chromatography (FPLC) studies indicated that both his-mms6 and c25-mms6 proteins were present in solution as multimers, thus potentially forming extended surfaces suitable for nucleation of magnetite. The significantly larger GST-mms6, which was found in a monomeric state and did not form multimers in solution, exhibited poor magnetite templating ability, and produced small nanoparticles lacking specific shape. This suggests that the ability of the protein to form multimers could play an important role in magnetite crystal formation, with larger numbers of protein molecules in the multimer resulting in the formation of larger magnetite nanoparticles. To test this hypothesis, we conducted magnetite synthesis in solution with various protein concentrations. In addition to synthesis in solution, we attempted synthesis on surfaces using both chemical ink-jet printing of protein solution on silicon wafers, as well as stamping the protein solution onto the surface of functionalized silicon. It was found that magnetite growth was limited to locations on the silicon wafer where protein had been stamped. The structure and placement of the formed magnetite nanoparticles were analyzed through electron microscopy and magnetic measurements. Additional magnetic analysis will offer further insight into the magnetic characteristics of mms6-assisted magnetite nanocrystals.

**Characterization of GaN, In<sub>0.25</sub>Ga<sub>0.75</sub>N and In<sub>0.50</sub>Ga<sub>0.50</sub>N for Photoelectrochemical Water Splitting.** SALLY PUSEDE (*University of Colorado at Denver and Health Sciences Center, Denver, CO*); TODD DEUTSCH (*National Renewable Energy Laboratory, Golden, CO*). GaN, In<sub>0.25</sub>Ga<sub>0.75</sub>N and In<sub>0.50</sub>Ga<sub>0.50</sub>N semiconductors were characterized as possible candidates for photoelectrochemical water splitting. The band gap energies of the materials were measured and found to decrease with increasing indium content. The flatband potential ( $V_{fb}$ ) of GaN was determined and the material's band edges verified to span the potentials of the hydrogen and oxygen evolution reactions; however, the  $V_{fb}$  positions of In<sub>0.25</sub>Ga<sub>0.75</sub>N and In<sub>0.50</sub>Ga<sub>0.50</sub>N could not be experimentally established. Two-electrode current density vs. potential measurements of both InGaN materials indicated anodic current flow at zero applied potential considerably below theoretical maxima, suggestive of photocorrosion rather than spontaneous water splitting. Where GaN was observed to be stable, In<sub>0.25</sub>Ga<sub>0.75</sub>N and In<sub>0.50</sub>Ga<sub>0.50</sub>N were found to be extremely susceptible to photocorrosion.

**A Radiochemical Separation of Selenium and Arsenic Using a BioRad Ag1-X8 Resin Column.** PAWAN RASTOGI (*Columbia University, New York, NY*); MICHAEL FASSBENDER (*Los Alamos National Laboratory, Los Alamos, NM*). Although classified as a group 1 carcinogen by the International Agency for Research on Cancer, arsenic and its compounds have proven to have many potential uses in nuclear medicine. Isotopes of arsenic, such as <sup>74</sup>As and <sup>72</sup>As, have been used in Positron Emission Tomography (PET). <sup>72</sup>As is a positron emitting isotope with a 26 hour half life (T) and mean positron energy (EB+mean) of 1.2 MeV. These characteristics lead <sup>72</sup>As to be a

promising candidate for being incorporated into radiopharmaceuticals. Such <sup>72</sup>As-labeled radiopharmaceuticals can be used in quantitative imaging of different biochemical and physiological processes. Here the delivery route for radioarsenic is considered via the production of a radionuclide generator parent like <sup>72</sup>Se, which, in turn, will decay into <sup>72</sup>As. A potential portable radioarsenic generator will be of value due to transportability and efficacy in delivering the radioisotopes to hospital and university settings. The main objective in this study was to develop an As/Se separation system that could be used in the future for a radionuclide medical generator. A strongly basic anion exchange resin (BioRad Ag1-X8) column was used to separate arsenic from selenium with different concentrations of ammonium chloride ( $\text{NH}_4\text{Cl}$ ). Radioarsenic was seen to elute with 0.01M  $\text{NH}_4\text{Cl}$  and 0.2M  $\text{NH}_4\text{Cl}$ . Generally all radioselenium retained on the column, but a small amount (~0.1%) was seen to elute with a 0.5M  $\text{NH}_4\text{Cl}$  eluent. The different retentions of radioarsenic and -selenium on the resin column support that more than one species of As and Se are present within the matrix. Due to time constraints speciation of the effluent was unable to be conducted. This preliminary separation of radiotracer quantities of arsenic and selenium shows much potential in developing a system fit for radionuclide generators. Future hopes include optimization of separation, characterizing the species involved in the matrix system, and development of a biologically deliverable form of the radioarsenic. The purpose of this paper is to report a method to separate arsenic from selenium using a BioRad Ag1-X8 anion exchange resin column with an ammonium chloride elution system.

**Increasing Activity for Oxygen Reduction of Cathode Electro-Catalysts in Fuel Cells.** JOSE REGALBUTO (*University of Illinois at Urbana-Champaign, Urbana, IL*); D.J. LIU (*Argonne National Laboratory, Argonne, IL*). As the search for alternatives to gasoline powered internal combustion engines intensifies, more attention is drawn to the use of fuel cells as an alternative power source. Fuel cells directly convert chemical to electrical energy, and are more efficient than internal combustion engines. The objective of our research is to identify and test new approaches in preparing electro-catalysts for use in fuel cells. We focused on two methods for the synthesis of cathode catalysts. The first was to steam activate a catalyst support before impregnating it with platinum. The second was to test a platinum free catalyst in basic media. A special emphasis was placed on using aligned carbon nanotubes as a catalyst support. Wet chemistry and gas phase vapor deposition methods were used to synthesize the catalysts. Our prepared catalysts were evaluated using standard electrochemical methods, with a focus on rotating disk electrode tests. We found that steam activation over a carbon nanotube support can improve oxygen reduction reaction (ORR) activity in acidic conditions. We also found that iron and nitrogen doped carbon nanotubes show good ORR activity in basic conditions. This work is part of a larger project to determine the feasibility of and make new catalysts for a direct ethanol fuel cell.

**\*Nanotechnology.** MELIXA RIVERA, MICHELLE ROSA (*University of Puerto Rico, Mayaguez, PR*); LUIS RIVERA, LUIS NUNEZ (*Argonne National Laboratory, Argonne, IL*). Due to its potential impact, nanotechnology has become an important part of research in fields such as physics, chemistry, and bioscience. One of the greatest advances made in nanoscience are nanoparticles which are currently being considered for drug delivery and for cancer treatment modality. Our project is focused on using PLGA (poly (lactic-co-glycolic acid)) nanoparticles for three different applications; systemic, local distribution and cellular drug delivery and for this matter these nanoparticles are being physically and chemically characterized. For the systemic application, tPA (tissue plasminogen activator), a clog buster, is the drug encapsulated in the nanoparticle. The core is surrounded by polymer with  $\text{Fe}_2\text{O}_3$  particle which makes it magnetic and easy to move them in different directions in the body. The tPA drug is useful because it destroys blood clots, and if we are able to deliver this drug successfully, it could save lives. For the tPA study, it is necessary to characterize the physical properties (size distribution and surface charge) and quantify the release of the drug from the nanoparticles. A spectrophotometer assay was performed to quantify the tPA released from the nanoparticles. For the local delivery application, the cancer drug encapsulated particles, the physical properties and drug release characteristics were examined and are critical for uniform distribution within a tumor. Size distributions were obtained using DLS (Dynamic light scattering) and a Zeta potential instrument. Zeta potential is a measure of the surface charge magnitude of the repulsion or attraction between particles. The 40–100 nm particles were encapsulated with a drug named TMZ (Temozolomide), used to treat two different types of brain tumor in adults: anaplastic astrocytoma and glioblastoma multiforme (GBM).



The nanoparticles were introduced in a rat's brain and using Convection Enhanced Delivery (CED) it was demonstrated that the particles were distributed uniformly along the brain. The cellular studies are based on selective liquids such as antibodies which will bind with over expressed receptors on cancer cells. The particles were ultracentrifuged to collect various size fractions which ranged from 200–250 nm and they are used for *in vitro* cell culture tests as a function of particle size. The concept of this experimental hypothesis is to see if the cancer cells can successfully uptake the nanoparticles over normal cells, and if the drug is delivered homogeneously.

**Silicon Nitride for Semiconductor Photoelectrochemical Water Splitting.** JOSEPH RYERSON (University of Colorado, Boulder, CO); JOHN TURNER (National Renewable Energy Laboratory, Golden, CO). Silicon nitride was analyzed to determine if it is an effective material to split water in direct photoelectrolysis application. Band gaps determined via photocurrent spectroscopy were found to exhibit indirect transitions between 1.54–1.75 eV. The higher end nitrogen content samples (14–16% nitrogen) fell within the band gap range effective in splitting water (1.7–2.2 eV). Flat band potentials were not negative enough to drive the hydrogen evolution reaction for these n-type films. Silicon nitride is therefore ineffective as a direct photoelectrolysis device, because its band edges are not aligned with respect to the redox potentials, a criteria necessary to generate hydrogen from water splitting. Twenty-four hour durability tests in 1M KOH revealed that this material is highly stable, as determined from post-test optical microscopic analysis, with low nitrogen contents (5%), and much less stable at higher nitrogen contents (14–16%N).

**Novel Bipolar Plate for Polymer Electrolyte Membrane Fuel Cells.** LILIA SANTOS (College of Dupage, Glen Ellyn, IL); J. DAVID CARTER (Argonne National Laboratory, Argonne, IL). Several partially fluorinated hydrocarbon polymers have been screened to form composite films as components of bipolar plates for application in proton exchange membrane fuel cells (PEMFC). Various compositions containing these polymers and graphite were scouted to prepare conductive films of about 0.4 mm thickness. A methodology was also devised to adhere these composites to the stainless steel substrate using anchoring molecules. The most promising anchor was found to be 4-[2,2,2-Trifluoro-1-(4-{2-hydroxy-3-[4-(4-oxiranylmethoxybenzyl)-phenoxy]-propoxy}-phenyl)-1-trifluoromethyl-ethyl]-phenol both pre- and *in-situ* prepared from bis (4-glycidyloxyphenyl)methane and 4,4'-(hexafluoroisopropylidene)diphenol. The composite films were consequently laminated on to 310S stainless steel plates using the anchors. These conductive composite coated plates showed excellent thermo-hydrolytic stability in boiling water for an extended period. In addition, resistance to delamination and corrosion were established by immersing these conductive plates in fairly concentrated H<sub>2</sub>SO<sub>4</sub> for 10 days. Out of several compositions evaluated, initial results indicate that poly(chlorotrifluoroethylene) with 60 volume% graphite to be a superior composition. These preliminary results are encouraging and would have positive impact on the cost factor of fuel cell assembly without sacrificing performance.

**Electron Transfer in Molecular Wires.** ELICIA SELVAGGIO (Dowling College, Oakdale, NY); JOHN MILLER (Brookhaven National Laboratory, Upton, NY). Conjugated oligofluorenes with two to ten monomer units (F2 to F10) were used to address fundamental questions regarding electron capture capacity and delocalization of charge. The oligofluorenes were reacted with sodium metal in tetrahydrofuran (THF) under vacuum, and ultraviolet/visible/near infrared (UV-vis-NIR) spectroscopy was used to measure the formation of anions, dianions, trianions, and tetranions. When reacted with sodium, F2 through F10 formed anions and dianions. Trianions and tetranions were observed in F4 and larger oligofluorenes. The absorption maxima, wavelengths at the maximum absorbances, and extinction coefficients were determined for each species formed. The study indicates that oligofluorenes can capture and store multiple electrons from sodium metal, and that the negatively-charged molecules are stable in the absence of air. Results for the series indicate that the length occupied by an electron is three to five monomer units. These results are consistent with the value obtained in polyfluorene by a different method in this lab. This challenges the notion that electrons are delocalized over the entire length of a conjugated molecule, and it has implications for understanding the fundamental nature of charged molecules in conjugated systems.

**Analysis of a Microbial Biofilm Matrix.** ANNA SIEBERS (University of California – San Diego, La Jolla, CA); MICHAEL P. THELEN (Lawrence Livermore National Laboratory, Livermore, CA). A matrix comprised of cells and polymeric substance distinguishes a robust biofilm

found floating in extremely acidic waters of an iron mine in northern California. Although both components are integral to the biofilm, the extracellular polymeric substance (EPS) has not been characterized and its function in the biofilm is poorly understood. To isolate the EPS, biofilm samples were disrupted and washed with dilute sulfuric acid. EPS could then be precipitated from the acid wash with either ammonium sulfate or ethanol. This gelatinous material was analyzed using a variety of independent techniques, including solvent treatment, UV-visible spectroscopy, gel electrophoresis, elemental analysis, and glycosyl analysis (in progress). EPS was not soluble in 17.5% NaOH, indicating a cellulosic component, and dissolved completely in 2M HCl. Analysis of material precipitated with 15, 30, 60 and 75% ethanol indicated differential sedimentation, with EPS primarily in the 15 and 30% fractions. Denaturing polyacrylamide gel electrophoresis of these fractions revealed two proteins with molecular weights of ~20 kDa and 60 kDa exclusively in the 60% fraction. Also, DNA was found in the same fraction using agarose gel electrophoresis; this was corroborated by a distinct absorbance peak at 260 nm. Elemental analysis of the total EPS material indicated a chemical formula of C<sub>18</sub>H<sub>35</sub>O<sub>17</sub>N<sub>2</sub>S, consistent with a polysaccharide assignment (1:2:1 CHO). Glycosyl analysis following pyrolysis, gas chromatography and mass spectrometry will determine the carbohydrate composition of the EPS and will give insight into its electronic charge state and hydrophobicity, and perhaps explain the buoyancy of the biofilm. We propose that the EPS protects the microbial community by buffering the acidity of the mine water and facilitating the exchange of gases at the air-water interface. Therefore, understanding the role of EPS within the biofilm will lead to further characterization of this unique microbial system and help determine how the community thrives in such an extreme environment.

**Dynamics of Fast Reactions in Ionic Liquids.** KATHRYN SIMS, KANDIS STUBBLEFIELD (Howard University, Washington, DC); JAMES F. WISHART (Brookhaven National Laboratory, Upton, NY). Ionic liquids (ILs) are liquids consisting of ions and have melting points below 100°C. Used in technologies and green chemistry they are being considered as processing media in the advanced nuclear fuel cycles needed to support a sustainable nuclear power industry for the world's future energy needs. It is important to understand the radiation-induced chemistry of ILs and how it may affect the chemistry of nuclear fuel separation. The unique reactivity of the "pre-solvated" electron surfaces as an important aspect of radiation chemistry due to the slower response to charge movement in ionic liquids relative to ordinary solvents. This study explores the reactivity of pre-solvated electrons in the ionic liquid N-methyl N-butylpyrrolidinium Ntf2 (P14NTf2) by measuring the kinetics of their reactions with cadmium, nitrate and selenate ions. These ions were selected because they show a wide range of reactivities with electrons in conventional solvents. The process of electron solvation, which competes with pre-solvated electron capture, is estimated by measuring the benzophenone anion solvation process because its spectroscopic properties are better suited to the available detection equipment than those of the electron. The Brookhaven National Laboratory (BNL) Laser Electron Accelerator Facility (LEAF) was used for all of the kinetics measurements performed by pulse radiolysis transient absorption spectroscopy. The C37 parameter was obtained to look at the lower concentration of benzophenone. Higher concentrations were also analyzed to allow us to look at the spectral shifts and compare them to that of the selected ions in the IL. In conclusion, we have determined the reaction kinetics of fast reactions in the IL.

**Dynamic Behavior of Nicotine and Its Impact on Assessment of Human Exposure to Secondhand Smoke.** EMMA SMITH (Yale University, Albany, CA); LARA GUNDEL (Lawrence Berkeley National Laboratory, Berkeley, CA). Secondhand tobacco smoke (SHS) is a common toxic contaminant in indoor air. Exposure to SHS has been linked to increased risk of lung cancer, asthma and acute respiratory illness. LBNL is currently measuring concentrations of SHS in bars and restaurants in Minneapolis-St. Paul, MN, in collaboration with colleagues at the Center for Energy and Environment. The goals are to correlate exposure data with health profiles of employees and assess the effects of prolonged indoor exposure to SHS. Measured concentrations of nicotine, 3-ethenyl pyridine and pyridine are being used as tracers of exposure. Nicotine is the most common tracer due to its uniqueness to tobacco, and its metabolite, cotinine, is a useful biomarker. However, earlier work at LBNL has shown that sampling nicotine in real environments is strongly influenced by changes between emission and collection, due to its affinity for surfaces (i.e., walls, clothes, hardware) and its reactivity (i.e., oxidation, acid-base reactions). This project measured the stability of gas-phase nicotine

in humid air and pure nitrogen, and dry air and nitrogen. High purity nicotine was injected into inert Tedlar bags and heated to vaporize it. Samples were collected after one, six and twenty-four hours, and analyzed using the same methods as the MN study (active sampling onto sorbent tubes, followed by gas chromatography with nitrogen-specific detection). After accounting for sorption of nicotine to the walls of the gas bags, the results showed that gaseous nicotine in dry N<sub>2</sub> remained stable, but samples of nicotine in humid air produced chromatograms with the same unusual features seen in field samples from MN, as well as peaks corresponding to the oxidation products nicotinaldehyde, N-methyl formamide, myosmine and cotinine. These data strongly suggest that nicotine oxidation is expedited over time in the presence of humid air. Thus, the degradation of nicotine either in the environment or inside sampling equipment may contribute to inaccurate concentration and exposure calculations. Future experiments are needed to monitor the behavior of nicotine for longer time periods, with varying amounts of nicotine and at different temperatures.

**Analysis of Compounds Produced by Biomass Burning Using High Resolution Mass Spectrometry.** *JEFFREY SMITH (University of Washington, Seattle, WA); JULIA LASKIN (Pacific Northwest National Laboratory, Richland, WA).* As global climate change becomes a pressing issue worldwide, it is important to identify the composition of particles emitted from biomass burning to understand the influence on our atmosphere from natural and anthropogenic pyrolysis. This study utilized high resolution mass spectrometry (MS) combined with electrospray ionization (ESI) for chemical characterization of smoke particles. The analyzed pyrolysis particles were collected on the six smallest particulate stages of a ten stage Micro-Orifice Uniform Deposit Impactor (MOUDI) using both Teflon and aluminum substrates. These substrates were then washed and filtered in solvents of both methanol and a 3:7 toluene:acetonitrile mixture. The samples were ionized using ESI, and analyzed in a high resolution hybrid linear ion trap Orbitrap instrument in both positive and negative ion modes. Tandem mass spectrometry (MS/MS) was performed for selected species to obtain more detailed structural information for specific compounds. Elemental composition was assigned to peaks based on their accurate mass-to-charge ratios. Comparison with literature data showed some overlap between the previously reported chemical components of smoke particles and species identified through the high resolution MS. Several known biomarkers for biomass pyrolysis, such as levoglucosan and dehydroabietic acid were observed in ESI-MS spectra. However, the high resolution MS identified many compounds not listed in existing literature publications; many of which contain nitrogen in their likely empirical assignments. These results indicate that the use of high resolution MS is a viable method for the analysis of compounds produced by biomass combustion, and can be used in conjunction with conventional approaches to obtain a more detailed characterization of the chemical composition of particulate matter emitted into the atmosphere during forest fires. Because this experiment only analyzed five biomass sources, substantial further research on a large variety of biomass burns will be needed to identify the majority of compounds produced through biomass combustion. Without first identifying the compounds produced by biomass combustion, it will not be known if these compounds pose risks to human health or potentially can affect the earth's climate.

**Automation of Chromatographic Separation Procedures.** *NICK STUCKERT (University of Wyoming, Laramie, WY); ROSI PAYNE (Pacific Northwest National Laboratory, Richland, WA).* The purpose of this paper is to provide a detailed discussion of an attempt to automate UTEVA and TRU gravity chromatographic separation procedures. These procedures are used for the chemical separation of radioactive elements prior to analysis. The problems that were encountered will be presented along with solutions and potential solutions to the problems. The methods for leak detection and resolution are presented in addition to a suite of additional minor changes. Some specific suggestions for modifications include the use of flow meters or creating an open system that relies on gravity filtration. In both cases substantial work will be required to develop a working system.

**Effect of Solvent Box Size on Wide-Angle X-Ray Scattering Patterns.** *HEATHER SUTTON (Chicago State University, Chicago, IL); DAVID M. TIEDE (Argonne National Laboratory, Argonne, IL).* Wide-angle X-ray scattering (WAXS) has been presented as an alternative method to the use of X-ray diffraction and nuclear magnetic resonance (NMR) for experimental structural verification of solution-phase macromolecular assemblies. Use of WAXS to determine solution structure requires comparison of the experimental scattering patterns to scattering patterns produced by molecular models. One approach

for producing these models is to use structures produced during explicit solvent molecular dynamics (MD) simulations. These simulations place the solute in a bath (a box or sphere shape is most common) of explicit solvent molecules. Prior work has focused on the solute scattering, removing all solvent molecules before the X-ray scattering pattern is computed, thus ignoring all solvent scattering. The long-term goal of this work is to extend the simulation model approach by including solvent in the scattering calculation in order to investigate the structure of solvent around porphyrin solutes. However, the finite size of the simulation solvent box results in artificial X-ray scattering. The present goal of this work is to facilitate treatment of solvent in MD simulations by determining adequate solvent box size to prevent the appearance of edge scattering peaks within our range of interest in the calculated scattering pattern. Solvate baths of various sizes and shapes were created using the solvate tool in visual molecular dynamics (VMD). After equilibration, constant energy (nve) simulations were run on these solvation boxes using the CHARMM force-field. Coordinates of these simulations were Fourier transformed to produce the calculated scattering patterns. These calculated scattering patterns have shown that the edge-scattering peaks can not be eliminated by increasing the size of the solvation box. However, spherical solvation baths have an analytic form for the edge scattering allowing the "false" scattering peaks to be subtracted off. These spherical baths will be used to study the solvent/solute interactions of porphyrin systems. Additionally, this work suggests that the TIP3 water model is accurate enough to use in further simulation work. In contrast, the charmm 22 toluene parameters will need to be adjusted before being used to model toluene/porphyrin interactions. The usage of WAXS data combined with simulation will provide, for the first time, a means to achieve this re-parameterization that is directly linked to experimental data.

**Electronic Characterization of Rare-Earth Doped Telluride Semiconductors.** *ERIK TOPP (Diablo Valley College, Pleasant Hill, CA); DALE L. PERRY (Lawrence Berkeley National Laboratory, Berkeley, CA).* Zinc telluride and telluride-containing compounds have been extensively analyzed by X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) in order to determine the chemical states and shifts in electronic energy levels of the elements present in the materials. To a lesser extent, chemical shifts of gadolinium lines in various compounds have also been studied. However, the characterization of ZnTe:Gd by XPS and AES is practically non-existent. Use of this material as a semiconductor in various applications requires that electrical contact be maintained between the material's surface and other electrical components. Buildup of oxides and other species on the surface can cause insulating effects, hampering the material's intended performance. It is, therefore, of interest to study surface reactions of the compound with air in order to identify surface product films that may adversely affect the utility of ZnTe:Gd as a multipurpose semiconductor. The current study was an initial characterization of these materials using XPS and AES. Observed spectra for the initial, "as received" surface yielded data consistent with the presence of Gd<sub>2</sub>O<sub>3</sub>, ZnO, and TeO<sub>2</sub>. Spectral parameters including binding energies, spin-orbit splitting, satellite structure, and kinetic energy Auger lines of elements compared favorably to analogous features in spectra of other Zn-Te-Gd compounds. Surface charging of the material was observed and studied in conjunction with argon ion sputtering. The results indicated that insulating surface films do indeed form on these materials in air, films that can act as interfacial layers between the semiconductor material and other materials such as electrical contacts attached to the surface of the semiconductor. A future examination of this material by other characterizing methods and types of instrumentation will provide further insight into the chemistry, structure, and electronic properties of this material and shed more light on the formation of the surface layers under ambient air exposure.

**\*Preparation and Properties of Phosphate Containing Ionic Liquids.** *KATHERINE URENA (Queens College, Flushing, NY); JAMES WISHART (Brookhaven National Laboratory, Upton, NY).* Research in the field of ionic liquids (ILs) continues to flourish due to their potential application in the area of green chemistry. ILs are organic salts with melting points below 100°C. Many of them exhibit melting points below room temperature and are referred to as room temperature ionic liquids. ILs are often composed of large organic cations and relatively small inorganic anions. Typical IL cations are nitrogen-containing and include imidazolium, pyridinium, and pyrrolidinium. This work focuses on the preparation and characterization of ILs based on these cations and the phosphate ( $\text{PO}_4^-$ ) anion. Data on the physical properties of phosphate ILs is lacking in the IL field. The need for specific structural types of ILs and data on their physical properties become more important as the



number of applications for ILs increase. The ILs were prepared by first preparing the quaternary ammonium halide salt precursors. The halide salts were made by reacting the tertiary amines with the alkyl halides in acetonitrile under reflux conditions. The halide salt precursors were then converted to phosphates using phosphoric acid in ethanol. The structures of the ILs were confirmed using nuclear magnetic resonance (NMR) spectroscopy. We have successfully synthesized pyrrolidinium and imidazolium based phosphate salts. Physical properties such as viscosity, conductivity and the thermal profiles of new salts will be reported.

**\*Effects of the Porphyrin Oxidation State on the Conformation of C-type Cytochromes.** *TIM VUONG (Chicago State University, Chicago, IL); KRISTY L. MARDIS (Argonne National Laboratory, Argonne, IL).* The increase in natural gas and oil prices has sparked renewed interest in alternative fuel sources such as solar energy. C-type cytochromes, found in a variety of bacteria, plants, and animals are being studied as possible building blocks for solar energy devices. Their usage depends on electron transfer (ET). To make these proteins suitable for ET devices, their solution conformation must be determined. Experimental wide-angle X-ray scattering (WAXS) studies have found that the c-type cytochrome (Protein Data Bank entry 1os6), extracted from the *Geobacter* genome and expressed in *Escherichia coli*, has identifiably different conformations in the reduced and oxidized form. The current work seeks to determine if the Chemistry of Harvard Molecular Modeling (CHARMM) force field can reproduce the experimental scattering pattern. This protein was chosen because (1) experimental scattering data are available and (2) it has three heme sites making the effect of oxidizing or reducing the iron in the center of the site larger than for proteins with single hemes. Calculations of the scattering profile were accomplished using structures obtained from crystal structure data. These starting structures were then subjected to nanosecond scale molecular dynamics simulations in a water sphere (radius = 30 Angstroms). The scattering profiles were obtained as the Fourier transform of the atomic coordinates. The scattering profiles calculated from the ensemble of structures for both the oxidized and reduced structures were then compared to the experimental data. Preliminary results indicate that the CHARMM 22 force field does distinguish between the oxidized and reduced forms of the protein. However, longer simulations are required before the results can be directly compared to experiment. The results will indicate the ability of the CHARMM forcefield to distinguish between two proteins differing only in the charge state of the irons in the three heme groups.

**Mechanization of Cadmium Sulfide Chemical Bath Deposition.** *DOMINIC WEBER (Colorado School of Mines, Golden, CO); STEVEN ROBBINS (National Renewable Energy Laboratory, Golden, CO).* The preferred method to deposit the Cadmium Sulfide (CdS) layer for thin-film solar cell research is Chemical Bath Deposition (CBD). In order to improve the reproducibility, and thus help the understanding of the process, a machine was created to mimic the CBD process. The design of the system involved placing the substrate over a flow well, only depositing CdS on one side of the substrate. Within the machine was a pump, designed to make the chemicals flow at a designated speed across the substrate. Also included was a temperature bath, designed to heat the chemicals to the desired deposition conditions. The machine was constructed, and everything in the system was tested for functionality. Since the machine was designed to mimic the current CBD method, the processed films were compared with CdS films made by the old process. These tests involved: thickness, thickness uniformity, and optical properties. The first run of the system revealed some major uniformity issues: the film had areas of no deposition (bubbles) on the edges and the thickness varied quite a bit on the other areas of the film. The first run also revealed another major problem: waste minimization. The run required 2.5 L (for 16 in<sup>2</sup> of substrate) compared to 500 mL (for 13.5 in<sup>2</sup>) in the old CBD method. The second run was devoted to waste minimization. A beaker was placed in the temperature bath to displace volume, reducing the amount of required chemicals to 1.5 L (for 36 in<sup>2</sup>). The second run showed that a smaller amount of liquid still produced a good quality film. Further designs for the CBD machine will have to concentrate on making the flow, and therefore the film thickness uniform. Future designs will also have to keep in mind the waste management issue: a great design would be one that uses 500 mL of solution or less.

**An Exploration of Ternary Compounds in RE-T-In, RE-T-Ge, and RE-T-Al Systems (RE = Ce, Nd, Lu; T = Pd, Pt, Ni): A New Ternary Indide and a Symmetry Question.** *JOSHUA WEBER (Grinnell College, Grinnell, IA); GORDON J. MILLER, SRINIVASA THIMMAIAH (Ames Laboratory, Ames, IA).* Ternary indides containing rare-earth (RE) and transition (T) metals, RE-T-In, have exhibited unique properties, yet

the characteristics of many RE-T-In systems remain unknown. This exploration initially focused on novel Ce-T-In systems, with T = Pd, Pt, and Ni. The focus then expanded to include ternary indides with the RE metals Nd and Lu and to include ternary compounds from RE-T-Ge and RE-T-Al systems to study the effects of varying atomic size and valence electron count. All samples were synthesized by arc-melting. A Guinier powder X-ray diffractometer was used for phase identification, and select samples were further analyzed using a Bruker single crystal X-ray diffractometer. Only select crystals were analyzed because most products, including all Ce-T-In systems, contained multiple phases instead of the desired complex-structured phase. The most interesting results have come from the Lu-Ni-In and Ce-Pd-Al systems, from the phases Lu<sub>10</sub>Ni<sub>10</sub>O<sub>8</sub>(1) In<sub>19</sub>O(1) and CePd<sub>0.93</sub>(1) Al<sub>3</sub>O<sub>8</sub>. Lu<sub>10</sub>Ni<sub>10</sub>O<sub>8</sub>(1) In<sub>19</sub>O(1) is a new phase. It crystallizes in the tetragonal crystal system, space group P4/nmm, adopting the Ho<sub>10</sub>Ni<sub>9</sub>In<sub>20</sub>-type structure, with unit cell parameters a = 13.128(1) Å and c = 8.977(1) Å, and unit cell volume of 1547.2(3) Å<sup>3</sup> for Z = 2. Single-crystal analysis indicates that CePd<sub>0.93</sub>(1) Al<sub>3</sub>O<sub>8</sub> belongs to space group I4/mmm, but it has been reported (as CePd<sub>0.75</sub>Al<sub>3</sub>.25) in space group I4mm. While electronic structure calculations seem to suggest this reported solution as well, the space group is still undetermined. The RF values of the refinement were 5.13% for Lu<sub>10</sub>Ni<sub>10</sub>O<sub>8</sub>(1) In<sub>19</sub>O(1) and 4.75% for CePd<sub>0.93</sub>(1) Al<sub>3</sub>O<sub>8</sub>. Physical measurements and electronic structure calculations will be used to study the new Lu-Ni-In compound and to resolve the space group problem of the Ce-Pd-Al compound. In future explorations, RE-T-In systems containing Nd, Lu, and other RE elements and additional RE-T-Ge and RE-T-Al systems, those systems which yielded the most interesting results, will be further investigated.

**A Search for Scintillators: Ce<sup>3+</sup> Doping of Alkali Gadolinium Halides and Eu<sup>2+</sup> Doping of Barium Zinc Oxides.** *LATORIA WIGGINS (North Carolina Agricultural and Technical State University, Greensboro, NC); STEPHEN DERENZO (Lawrence Berkeley National Laboratory, Berkeley, CA).* The need for new and improved gamma ray and X-ray detectors, scintillators, is at an all time high due a progression in detection knowledge. Commonly used scintillators such as BGO and YAP have undesirable properties such as low luminosity, and slow decay times. The mission of the High Throughput Characterization and Synthesis Facility (HTCSF) is to develop scintillators with rapid decay times, high luminosities and crystal production at low costs. Discovering new scintillators required literature searches, synthesizing and the characterization of compounds. The research at hand concentrated on cerium (III) doped alkali halides and europium (II) doped barium zinc oxides. Compounds were synthesized using the ceramic method mostly performed in a nitrogen filled glove box because of the hygroscopic nature of the halides. Characterization consisted of X-ray diffraction, X-ray luminescence and pulsed X-ray measurements. Several new inorganic scintillators were founded, however, findings concerning barium zinc oxide synthesis warrant further investigation of the compound.

## Computer Science

**A Case Study of Efficient Social Network Simulation through General Processing on Graphics Processing Units.** *BRANDON AABY (Maryville College, Maryville, TN); KALYAN S. PERUMALLA (Oak Ridge National Laboratory, Oak Ridge, TN).* Agent based simulation has been both a large area of study and a widely used tool for scientific research in past years. Current implementations run on standard CPUs, and with the requirement of processing ever growing data sets, higher computational speed is of the utmost importance. General processing on graphics processing units (GPGPU) is an emerging platform offering the possibility of increased speed for data sets and models that can be processed in parallel. Agent based simulation is one such candidate for performance gains in a GPGPU implementation. My research has focused on thoroughly investigating GPGPU's suitability for providing researchers with a more efficient way of conducting agent based simulation research. Studies were done using two conventional models: two-dimensional diffusion and Conway's Game of Life. I first created an optimized CPU diffusion model and, following a determination of accuracy, compared computational speed with an Open Graphics Library GPGPU implementation previously developed at Oak Ridge National Laboratory. Similarly, like studies were completed with the Game of Life. Following this strict CPU and GPGPU comparison, further comparisons and analyses were conducted with a widely used agent based simulation API, Repast. Evaluations involving Repast revolved around the premise that were GPGPU to be harnessed by researchers for agent based simulation, it must be competitive with currently used research technologies.